# PHYSICAL CHEMISTRY

GENERAL EDITOR Ya. GERASIMOV

VOLUME 2

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# PHYSICAL CHEMISTRY

*Edited*
by
Prof. Ya. GERASIMOV,
Corr. Member, USSR Acad. Sc.

VOLUME 1

Fundamentals of Termodynamics
Thermodynamics of Solutions
Chemical Eguilibria
Chemical Thermodynamics
Heterogeneous Phase Equilibria
Surface Phenomena. Adsorption
Gas Chromatography

VOLUME 2

Kinetics of Chemical Reactions
Chain Reactions
Reactions In Electrical Discharges
Catalytic Reactions
Electrochemistry
Electromotive Forces
Chemical Sources of Current

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Я. ГЕРАСИМОВ, В. ДРЕВИНГ, Е. ЕРЕМИН, А. КИСЕЛЕВ,
В. ЛЕБЕДЕВ, Г. ПАНЧЕНКОВ, А. ШЛЫГИН

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YA. GERASIMOV, V. DREVING, E. EREMIN, A. KISELEV,
V. LEBEDEV, G. PANCHENKOV, A. SHLYGIN

# PHYSICAL CHEMISTRY

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CORR. MEMBER, USSR ACAD. SC.

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**This book is the second volume of a university course in physical chemistry, and deals with the fundamentals of chemical kinetics, catalysis and electrochemistry.**

**It is designed for students of chemical faculties of universities. It will also be useful for postgraduate students and teachers of physical chemistry.**

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# SYMBOLS[1]

*A* activity of catalyst; area; constant; Helmholtz energy; mass of gramme-ion; mass efficiency of catalyst

*a* activity; amount of substance; mean effective diameter of ions; number of gramme-atoms per mole; number of molecules of product; specific activity of catalyst

*B* constant

*b* amount of substance

*C* capacitance; constant

*c* amount of poison adsorbed by catalyst; cell constant; concentration; velocity of light

*D* absorbed radiation dose; diffusion coefficient; energy of dissociation

*d* distance; path of ionizing particle in irradiated substance

**E** electric field strength

*E* activation energy; e.m.f.; energy; potential difference; potential gradient

*e* base of natural (Naperian) logarithms; charge of electron [2]; charge of particle; electron

*F* Faraday constant; force

*f* activity coefficient, mole-volume concentration basis; activity function of water ions; force; force constant; fugacity

*G* conductance; Gibbs energy; radiation-chemical yield

*H* enthalpy; heat of reaction

*I* current intensity; energy of ionization; induction factor; intensity of light; ionic strength of solution; ionization potential; moment of inertia

*i* empirical coefficient

*J* rate of reaction

*j* current density

*K* activity product; cell constant; dissociation constant; electrolytic dissociation constant; equilibrium constant; hydrolysis constant; ionic product of water; relative temperature coefficient of conductivity; solubility product

*k* Boltzmann constant; difference between standard potentials; rate constant [1]; dissociation function; molecule adsorption coefficient

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[1] In the English translation of this book the recommendations contained in the *Manual of Symbols and Terminology for Physicochemical Quantities and Units* adopted by the IUPAC Council at Cortina d'Ampezzo, Italy, on July 7, 1969 (see *Pure and Applied Chemistry*, Vol. 21, No. 1, 1970) have been used wherever possible. —*Translator's note*.

[2] The symbol $q_e$ is used when necessary to avoid confusion with the symbol *e* for the base of natural logarithms.

[1] The symbol $k_r$ is used instead of *k* when necessary to avoid confusion with the symbol *k* for the Boltzmann constant.

| | |
|---|---|
| $L$ | constant; length of chain |
| $l$ | critical distance; distance from beginning of reaction zone; length; thickness of diffuse layer |
| $M$ | mass of mole; molecular mass |
| $m$ | mass; number of molecules; rate of flow of mercury |
| $N$ | number of molecules; number of particles |
| $N_A$ | Avogadro constant |
| $n$ | amount of substance; number of gramme-ions; number of kilomoles; number of molecules of intermediate; order of reaction with respect to intermediate; quantum number |
| $P$ | decrease in electrolyte; impulse of rotation; probability; steric factor; total pressure |
| $p$ | dipole moment; impulse; power of adsorbed radiation dose; pressure |
| $\bar{p}$ | momentum |
| $Q$ | heat; partition function; quantity of heat; quantity of light |
| $\bar{Q}$ | heat effect of reaction |
| $q$ | electric charge |
| $R$ | gas constant; resistance |
| $r$ | activity of one $n$-atomic ensemble; distance between ions; distance between particle centres; total content of isotope molecules in a given system |
| $S$ | entropy; surface |
| $s$ | factor |
| $T$ | absolute temperature |
| $t$ | temperature, °C; time; transport number |
| $U$ | internal energy; mobility of ion; potential difference |
| $u$ | absolute mobility; concentration of intermediate; linear velocity; power of electrical discharge |
| $u'$ | velocity of cation |
| $V$ | mobility of ion; rate of flow of a gas; relative velocity of molecule; Volta potential; volume |
| $v$ | absolute mobility; partial volume of solvent in solution; velocity; volume of mole |
| $v'$ | velocity of anion |
| $W$ | work |
| $x$ | degree of transformation (amount of reacted substance); mole fraction (amount of substance in moles) |
| $Z$ | number of collisions; number of migration regions; number of molecules |
| $z$ | charge number (charge of ion); factor |
| $\alpha$ (alpha) | anharmonic ratio; coefficient; degree of dissociation; factor; heat transfer coefficient; most probable velocity of molecule; poisoning coefficient; probability; single separation coefficient |
| $\beta$ (beta) | constant; diffusion rate constant; fraction hydrolyzed |
| $\gamma$ (gamma) | activity coefficient; interfacial tension; quantum yield; temperature coefficient of reaction rate |
| $\Delta$ (delta) | degree of transformation; Lalacian operator; mean migration area |
| $\delta$ | distance; interval; probability of a cycle; thickness |
| $\varepsilon$ (epsilon) | energy of molecule; energy required for photochemical dissociation; liquid junction potential; relative permittivity |
| $\eta$ (eta) | overvoltage; thermal efficiency; viscosity; viscosity factor |
| $\theta$ (theta) | fractional (surface) coverage |
| $\varkappa$ (kappa) | conductivity; factor; number of intermediate molecules |
| $\Lambda$ (lamba) | equivalent conductivity |
| $\lambda$ | heat of adsorption; mean free path of molecule; wavelength |
| $\mu$ (mu) | chemical potential;dipole moment of molecule; number of primary elementary reactions; reduced mass of molecule |
| $\nu$ (nu) | electrochemical potential; frequency; latitude; number of catalyst atoms per migration region; number of ions in dissociation of a molecule; |

| | |
|---|---|
| | stoichiometric coefficient |
| $\Pi$ (pi) | osmotic pressure; product |
| $\pi$ | ratio of circumference to diameter of circle, 3.14159 |
| $\rho$ (rho) | charge density; density; resistivity |
| $\Sigma$ (sigma) | sum |
| $\sigma$ | collision diameter; diameter of a molecule; surface charge density; surface tension; symmetry number of molecule; wave number |
| $\tau$ (tau) | half-life; life of mercury drop; lifetime of molecule; time; true trasport number |
| $\varphi$ (phi) | angle; dilution of solution; longitude; potential; potential difference (jump) |
| $\chi$ (chi) | transmission coefficient |
| $\psi$ (psi) | apparent volume; potential |
| $\omega$ (omega) | angular velocity; fundamental frequency of vibrations; number of new molecules formed by one molecule of intermediate |

The superscript ° (for example $G°$) on a thermodynamic function means that the substance is in its standard state.

The Greek letter $\Delta$ in front of a thermodynamic function (for example $\Delta G$) means that the change (final minus initial) is referred to.

# PREFACE

The present textbook is the second volume of a two-volume course prepared by a group of lecturers from the physical chemistry department of the chemical faculty of the Lomonosov State University (Moscow).

The second volume includes the fundamentals of chemical kinetics, catalysis and electrochemistry. The authors of the second volume are G. M. Panchenkov (Chapters 1, 2, 5, 8, 9, 11 and 14, Secs. 7.4 and 12.9 to 12.13), E. I. Eremin (Chapters 3 and 10), Ya. I. Gerasimov (Chapters 15, 16, 19-23), A. I. Shlygin (Chapters 17 and 24), V. P. Dreving (Chapter 18), and the late V. P. Lebedev (Chapters 4, 6, 7, 13 and Secs. 12.1 to 12.8).

The two volumes of *Physical Chemistry* include all the sections of the corresponding course envisaged by the syllabus for chemical faculties of universities. The structure of matter is not considered in the present course, since chemical faculties have separate courses in *The Structure of Molecules* and *Crystallo-Chemistry*.

The sections of the book designated by asterisks, and also the parts of other sections printed in small type, may be omitted when studying physical chemistry according to a required syllabus. This additional material, which is set out in the same comprehensible manner as the main part of the course, can be used for a more detailed study of the subject.

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# KINETICS OF CHEMICAL REACTIONS

## CHAPTER 1

## FORMAL KINETICS

The branch of physical chemistry devoted to the laws of chemical reactions in time is called *chemical kinetics.*

One of the tasks of chemical kinetics is a quantitative description of the course of a chemical reaction in time at a constant temperature depending on the concentrations of the reactants. The relevant mathematical relationships are derived with the aid of the fundamental postulate of chemical kinetics (see Sec. 1.1). The branch of chemical kinetics dealing with these topics is called *formal kinetics.*

**1.1. Rate of a Chemical Reaction.** A chemical reaction can be written in the general form as follows:

$$\nu_1 A_1 + \nu_2 A_2 + \ldots + \nu_n A_n \longrightarrow \nu_1' A_1' + \nu_2' A_2' + \ldots + \nu_n' A_n' \qquad (1.1)$$

where $\nu_i$ and $\nu_i'$ = stoichiometric coefficients of the reactants and products

$A_i$ and $A_i'$ = reactants and products.

*The number of molecules of a given species reacting in a unit of time is called the rate of a chemical reaction.*

To be able to compare the rates of different reactions, it is convenient to relate them to a unit of volume. For this reason for calculations and comparison of the rates of reactions, the latter are determined as the number of molecules or moles of a given substance reacting in a unit of volume per unit of time.

To find the rate of a chemical reaction it is sufficient to know the change in the concentration of one of the substances participating in it (a reactant or product) in time, since the change in the amounts of all the remaining substances can be determined from Eq. (1.1).

Chemical reactions rarely proceed in one stage in the way it is the accepted practice to write them in chemistry textbooks. In a customary single-stage equation of a chemical reaction, only the initial and final states are indicated. Such an equation can be considered as a symbolic expression of the material balance (the law of conservation of matter). Actually a reaction proceeds through a number of intermediate stages. In the majority of cases we do not know the detailed mechanism of a reaction owing to the great difficulties in establishing the intermediates. The rate of the summary reaction, which, as has already been indicated, is found according to the reduction in the amount of one of the reactants or the growth in the amount of one of the products per unit of time in a unit of volume, is determined by the rate of the slowest stage. In general it can be assumed that the rate of a chemical reaction is directly proportional to the concentrations of the reactants to certain powers, i.e. for reaction (1.1) we have

$$J = kc_{A_1}^{n_1} c_{A_2}^{n_2} \ldots c_{A_n}^{n_n} \tag{1.2}$$

where $J$ = rate of a chemical reaction
$c_{A_i}$ = concentrations of the reactants
$k$ = constant of reaction rate
$n_i$ = order of the reaction with respect to a given substance (see Sec. 1.3).

Only when a reaction proceeds in one stage does the order of the reaction with respect to a given substance coincide with the stoichiometric coefficient of this substance in chemical equation (1.1). It is important to note that $n_i = \nu_i$ for all reactions that proceed infinitely slowly in conditions infinitely close to a state of chemical equilibrium regardless of the fact that in conditions far from equilibrium they may proceed through a number of intermediate stages. This is explained by the circumstance that a chemical reaction proceeds through such a set of intermediate reactions which in the given conditions ensures their highest rate. In other words, it ensures the greatest probability of reaching the final state. Should a chemical system be in a state infinitely close to that of chemical equilibrium, it proceeds, as noted above, infinitely slowly, and for this reason it may proceed along a hardly probable path, i.e. directly in one stage.

Equation (1.2) is sometimes called the *fundamental postulate of chemical kinetics*. The physical meaning of the constant $k$ can be established if we assume that all the concentrations are equal to unity, i.e. $c_{A_1} = c_{A_2} = \ldots = c_{A_n} = 1$, whence

$$J = k \tag{1.3}$$

i.e. *the constant of the rate of a chemical reaction is the rate of a reaction on condition that the concentrations of the reactants are equal to unity.* This quantity is sometimes called the *specific rate of a chemical reaction.*

A glance at Eq. (1.2) shows that the rate of a reaction is a function of time, since the amounts of the reactants change with time. For this reason we can introduce the concept of the mean rate of a reaction $\bar{J}$:

$$\bar{J} = -\frac{n''_{A_i} - n'_{A_i}}{V(t'' - t')} \tag{1.4}$$

where $n'_{A_i}$ and $n''_{A_i}$ = numbers of moles of one of the reactants at the initial $t'$ and final $t''$ moments of time

$V$ = volume of system under consideration.

The minus sign appears in the right-hand part because the rate of a chemical reaction can only be a positive quantity. Since we are considering a reaction proceeding from the left to the right, $n''_{A_i} < n'_{A_i}$, and therefore $J > 0$, i.e. it is a positive quantity.

If $t'' - t'$ tends to zero, we get the true rate $J$, which is the rate of the reaction at the given moment:

$$J = -\frac{1}{V}\frac{dn_{A_i}}{dt} \tag{1.5}$$

If the volume being considered is constant, it can be introduced under the sign of the differential, and

$$J = -\left(\frac{\partial c_{A_i}}{\partial t}\right)_V \tag{1.6}$$

It is convenient to use Eq. (1.6) in dealing with reactions in solutions, since we may frequently neglect the change in the volume of the solution as a result of the reaction.

**1.2. Opposing and Concurrent (Reversible and Irreversible) Reactions.** From the statistical viewpoint all chemical reactions simultaneously proceed in the direction of equilibrium and in the opposite direction. The rate of a reaction in the direction of equilibrium is greater than that in the opposite one, and as a result the system approaches equilibrium. In equilibrium both reactions have the same rates, so that the rate of the summary process is equal to zero. Thus, in the general case chemical reactions are opposing (two-way) ones or, as is frequently said, *reversible* ones. The concept *reversible reaction* in the above meaning should be distinguished from the thermodynamic concept *reversible process* (see Vol. 1, Sec. 1.6). The latter is characterized by an infinitely small difference between the rates of the forward and backward processes and, consequently, by an infinitely low rate of the resulting process and an infinitely small deviation of the system from equilibrium.

A two-way chemical reaction, naturally, is reversible in the thermodynamic sense only in direct proximity to the state of chemical equilibrium. A two-way reaction in a state far from the equilibrium one, when the rates of the forward and reverse processes appreciably differ and the summary (resultant) rate of the reaction considerably differs from zero, is thermodynamically irreversible. The sphere of application of the concept *two-way reaction* (or *opposing reactions*) is broader than the thermodynamic concept *reversible reaction*. Consequently the former term should be adhered to for real reactions. The term *reversible reaction*, however, has gained much ground in the broad, not thermodynamic, meaning, and we have to use it with a view to what has been said above.

As already indicated, all chemical reactions are in principle two-way (reversible) ones. Practically, however, in the conditions in which a given kinetic experiment is conducted (the initial concentrations, temperature, pressure), equilibrium may be so shifted that only the products can be detected analytically, and the concentrations of the reactants are so small that they may be neglected. Here practically only the forward process proceeds. Such reactions have been called *kinetically one-way* or *kinetically irreversible* reactions. Usually these are reactions in the course of which at least one of the products leaves the sphere of the reaction (for example, in a solution reaction, the product precipitates or is liberated in the form of a gas), or which are accompanied by a great positive heat. Ionic reactions are practically irreversible if one of the products is a poorly soluble or poorly dissociated substance.

If in conducting a reaction, sufficiently great, analytically determinable concentrations of both the reactants and products correspond to equilibrium, then only at concentrations sufficiently far from the equilibrium ones (at low concentrations of the products) is it possible with a certain approximation to neglect the rate of the reverse process. The closer the process is to equilibrium, the more will the reverse reaction affect the kinetics of the process as a whole. Chemical reactions in which it is necessary to take into consideration the rates of the forward and reverse reactions simultaneously and independently proceeding in opposite directions, are called *kinetically two-way* (*opposing*) or *kinetically reversible* ones.

In this part of the book we shall call kinetically two-way reactions reversible ones, and kinetically one-way reactions irreversible ones.

**1.3. Kinetic Classification, Molecularity and Order of Reactions.** Chemical reactions can be classified according to the number of molecules participating in each elementary chemical act. This number is called the *molecularity* of the reaction; it must be an integral number. Reactions in which such an act is the chemical transformation of one molecule (isomerization of a molecule, its dissociation into several

molecules containing a smaller number of atoms, etc.) are called *monomolecular*. In *bimolecular* reactions an elementary act occurs upon the collision of two molecules (different or the same), and in *trimolecular* ones upon the collision of three molecules. Since at normal pressure triple collisions are much less frequent than double ones, trimolecular reactions (for example, the reaction of nitrogen oxide with oxygen and halides, stabilization in the bulk recombination of radicals) are quite rare in comparison with bimolecular ones. Reactions with a greater molecularity are practically not encountered.

Direct experimental investigation of the kinetics of a chemical reaction only in exclusive cases allows us to relate it to one of the groups indicated above. It is possible to do this only for the so-called *simple* reactions proceeding in one stage whose equation coincides with the stoichiometric equation of the reaction as a whole (for example, the decomposition and synthesis of hydrogen iodide, the decomposition of nitrogen dioxide and nitrosyl chloride, and some other reactions). Most chemical reactions, however, are a combination of several consecutive (or sometimes parallel) elementary reactions, each of which may belong to any of the kinetic groups indicated above. This circumstance inevitably introduces complications into the kinetics of a process as a whole. In the simplest case, if one of the elementary reactions proceeds much slower than the others, the kinetic law observed will correspond to this reaction, and to no other one. If the rates of the elementary reactions are comparable, experimental kinetics may be even more complicated.

Owing to the multiple-state nature of the majority of chemical processes, even a chance coincidence of a kinetic law being observed with the law of a monomolecular, bimolecular, etc., reaction cannot yet serve as a proof of the truth of the reaction mechanism. This is why the concept of the *order of a reaction*, differing in principle from the concept of *molecularity*, has been introduced to characterize the kinetics of experimentally studied processes.

The *order of a chemical reaction with respect to a given substance* is a number equal to the exponent $n_i$ of the concentration factor of this substance in kinetic equation of the reaction (1.2). The sum of the exponents $n_1 + n_2 + \ldots + n_n$ of the concentrations of all the reactants in the kinetic equation (1.2) determines the *order of a reaction as a whole.*

Owing to the complicated nature of the majority of chemical processes, the order of a reaction only in some instances is that which could be expected on the basis of the stoichiometric equation of the reaction. This is true in the form of a chance coincidence only for simple reactions, for example for the reaction of decomposition of nitrosyl chloride or the synthesis of hydrogen iodide:

$$2NOCl = 2NO + Cl_2 \text{ and } H_2 + I_2 = 2HI$$

Ordinarily the order of a reaction does not coincide with its molecularity and does not correspond to the stoichiometric equation. Thus, the synthesis of hydrogen bromide

$$H_2 + Br_2 = 2HBr$$

according to the stoichiometric equation ought to proceed as a reaction of the second order. But since this reaction is a complicated one proceeding in at least five stages, its mechanism is also quite complicated. The rate of the reaction is found to be directly proportional to the first power of the concentration of hydrogen (a reaction of the first order with respect to hydrogen), to a fractional power of the concentration of bromine and inversely proportional to the concentration of hydrogen bromide. Thus, a process that is simple from the stoichiometric viewpoint is found to be a reaction of a fractional order from the kinetic one. The reaction

$$6FeCl_2 + KClO_3 + 6HCl = 6FeCl_3 + KCl + 3H_2O$$

should be of the thirteenth order according to the stoichiometric equation, but kinetically it satisfies the equation of a third-order reaction. We can give a very great number of similar examples.

Thus the order of a reaction characterizes the formal-kinetic dependence of its rate on the concentration of the reactants, and its molecularity—the elementary mechanism of the separate stages of a complicated process. These concepts coincide only for reactions having a simple mechanism.

## *Kinetics of Reactions in Static Systems*

One of the methods of studying the kinetics of chemical reactions is the conducting of a reaction in a closed vessel, i.e. at constant volume. Such conditions, in contrast to ones when the reaction mixture continuously flows through the reaction space, are called *static* ones.

**1.4. Irreversible Reaction of the First Order.** The following are examples of these reactions:

the reaction of decomposition of azomethane

$$CH_3N_2CH_3 \rightarrow C_2H_6 + N_2$$

the reaction of decomposition of nitrogen pentoxide

$$2N_2O_5 \rightarrow O_2 + 2N_2O_4$$

the reaction of decomposition of dimethyl ether

$$CH_3OCH_3 \rightarrow CH_4 + H_2 + CO$$

The kinetic equation of a first-order reaction can be deduced as follows. Assume that at the initial moment we have $a$ moles of reac-

tant A. If by the time $t$ the number of moles of the substance that have reacted is $x$, then $(a - x)$ moles remain in the mixture. The concentration of substance A by the time $t$ will thus be

$$c_A = \frac{a-x}{V} \tag{1.7}$$

where $V$ is the volume of the system.

According to the definition, the rate of a first-order reaction is directly proportional to the concentration of the reactant to the first power. Consequently, from basic kinetic equation (1.2), with account taken of Eq. (1.5), we get

$$-\frac{d(a-x)}{V\,dt} = \frac{k}{V}(a-x) \tag{1.8}$$

Cancelling $V$ in both parts of the equation, we have

$$\frac{dx}{dt} = k(a-x) \tag{1.8a}$$

This is a differential equation of the rate of a first-order irreversible reaction. Separating variables, we get

$$\frac{dx}{a-x} = k\,dt \tag{1.9}$$

Integration yields

$$-\ln(a-x) = kt + C \tag{1.10}$$

We can find the integration constant $C$ by inserting the initial conditions ($t = 0$ and $x = 0$) into Eq. (1.10):

$$-\ln a = C \tag{1.11}$$

Inserting Eq. (1.11) into Eq. (1.10) and solving the latter with respect to $k$, we obtain

$$k = \frac{1}{t}\ln\frac{a}{a-x} \tag{1.12}$$

Equation (1.12), by dividing the numerator and denominator of the fraction after the logarithm sign by the volume (on condition that it is constant), can be rewritten as follows:

$$k = \frac{1}{t}\ln\frac{c_0}{c} \tag{1.12a}$$

where $c_0$ = initial concentration of the reactant
$c$ = concentration of this substance by the moment of time $t$.

As can be seen from Eqs. (1.12) and (1.12a), the quantity $k$ has the dimension of the inverse time $t^{-1}$.

Consequently, the rate constant of a first-order reaction can be expressed in $s^{-1}$, $min^{-1}$ or $h^{-1}$.

TABLE 1.1

**Calculation of Rate Constant for the Decomposition of Hexaphenyl Ethane Dissolved in Chloroform**

$$(C_6H_5)_3C-C(C_6H_5)_3 \longrightarrow 2(C_6H_5)_3C$$

| $t$, min | $c$, relative concentration | $k\times10$ min$^{-1}$ | |
|---|---|---|---|
| | | $-\frac{\Delta c}{\Delta t}\frac{1}{c_{mean}}$ | $\frac{1}{t}\ln\frac{c_0}{c}$ |
| 0.00 | 1.000 | 2.03 | |
| 0.15 | 0.970 | 2.24 | 2.03 |
| 0.43 | 0.912 | 2.08 | 2.13 |
| 0.75 | 0.854 | — | 2.10 |
| 2.70 | 0.559 | 1.94 | 2.15 |
| 3.20 | 0.500 | 2.19 | 2.16 |
| 3.78 | 0.442 | 2.16 | 2.16 |
| 5.67 | 0.294 | 2.11 | 2.16 |
| 6.69 | 0.235 | — | 2.11 |
| 8.68 | 0.147 | 2.45 | 2.20 |
| 10.88 | 0.088 | 3.00 | 2.23 |
| 14.90 | 0.030 | | 2.30 |

Equation (1.12a) is used in calculating the rate constant for the reaction of decomposition of hexaphenyl ethane (Table 1.1, column 4). Column 3 gives the values of the rate constant calculated from the equation of the rate of a first-order reaction written as follows:

$$-\frac{\Delta c}{\Delta t}=kc_{mean} \tag{1.13}$$

Elimination of the logarithm in Eq. (1.12) yields

$$\frac{a}{a-x}=e^{kt} \tag{1.14}$$

whence

$$a-x=ae^{-kt} \tag{1.15}$$

and

$$x=a(1-e^{-kt}) \tag{1.16}$$

Equation (1.15) can be used to determine the amount $(a-x)$ of substance A that has not reacted by the time $t$, and Eq. (1.16)—the amount $x$ of this substance that has reacted by the time $t$ or, in other words, the amount of substance B formed by the time $t$.

The dependence on time of the reacted $x$ and remaining $a-x$ amount of the initial substance A is shown graphically in Fig. 1.1.

It can be seen from the figure and from Eqs. (1.15) and (1.16) that the initial substance will completely disappear in an infinitely great interval of time. In practical calculations a reaction is assumed to terminate at the moment when it is impossible to detect the initial

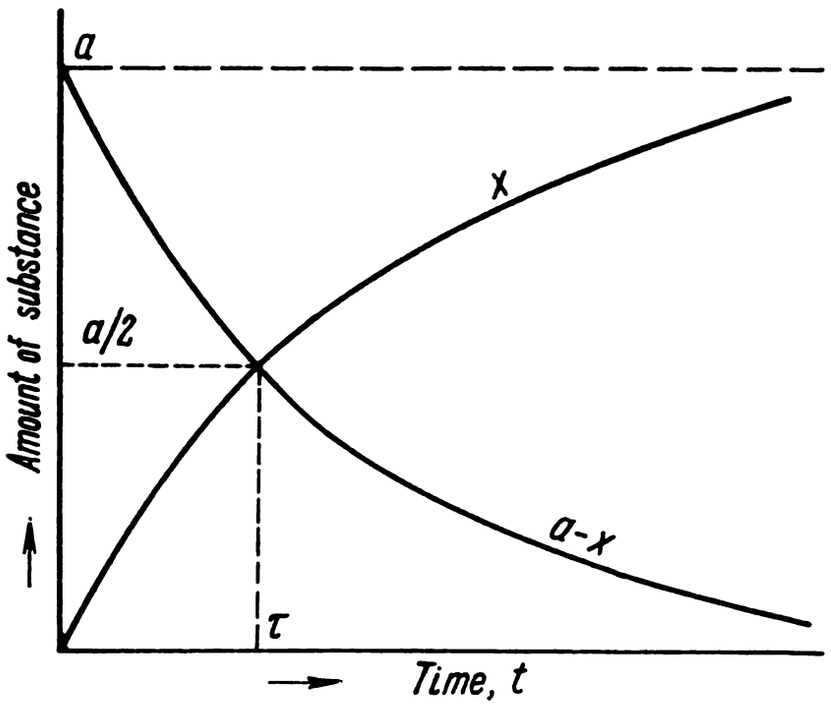


Fig. 1.1. Change in amount of remaining and formed substance with time for a monomolecular reaction

substance analytically. The time corresponding to the point of intersection of the curves is designated by $\tau$. It is obvious that at the point of intersection

$$a - x = x \quad \text{or} \quad x = \frac{a}{2} \tag{1.17}$$

i.e. by the time $\tau$ half of the initial substance will react. For this reason the time $\tau$ is called the *half-life*. With account taken of Eq. (1.17), from Eqs. (1.15) and (1.16) we get

$$ae^{-k\tau} = a(1 - e^{-k\tau})$$

or

$$2e^{-k\tau} = 1$$

whence

$$e^{k\tau} = 2$$

or

$$\tau = \frac{\ln 2}{k} \tag{1.18}$$

Thus the half-life does not depend on the amount of the initial substance. This is obvious for simple monomolecular reactions, since the transformation of the molecules in these reactions is spontaneous (it does not depend on the presence of the remaining ones).

The reciprocal of the rate constant of a monomolecular reaction (a simple first-order reaction) characterizes the mean lifetime of the separate molecules. Indeed, the mean lifetime of a separate molecule can be found if we assume that

$$\bar{\tau} = \frac{\int_0^\infty t\,dN}{N_0} \tag{1.19}$$

where $t$ = lifetime of a separate molecule
$N_0$ = total number of molecules.

But

$$dN = kN\,dt \tag{1.20}$$

whence

$$N = N_0 e^{-kt} \tag{1.21}$$

Consequently

$$dN = kN_0 e^{-kt}\,dt \tag{1.22}$$

Inserting Eq. (1.22) into Eq. (1.19) and integrating in the latter by parts ($t = u$ and $e^{-kt}\,dt = dv$), we get

$$\bar{\tau} = k\int_0^\infty te^{-kt}\,dt = k\left[-t\frac{1}{k}e^{-kt}\right]_0^\infty - k\int_0^\infty \frac{1}{k}e^{-kt}\,dt = -\frac{1}{k}e^{-kt}\Big|_0^\infty = \frac{1}{k} \tag{1.23}$$

It follows from Eq. (1.23) that the mean lifetime of one molecule is the reciprocal of the rate constant of a monomolecular reaction.

**1.5. Irreversible Reaction of the Second Order.** The saponification of an ester with an alkali can serve as an example of a second-order reaction

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

In the general form an irreversible second-order reaction is described by the stoichiometric equation

$$A + B \rightarrow C + D + \ldots$$

Let us assume that we have $a$ moles of substance A and $b$ moles of substance B at the moment of time $t = 0$, and that $x$ moles of substance A have reacted by the moment $t$. From the equation of the reaction it is clear that $x$ moles of substance B will also have reacted, i.e. $a - x$ moles of substance A and $b - x$ moles of substance B will have remained unreacted by the moment $t$. If the volume of the system is $V$, then according to Eqs. (1.2) and (1.5) the rate of the reaction can be written as follows:

$$-\frac{d(a-x)}{V\,dt} = k'\,\frac{a-x}{V}\,\frac{b-x}{V} \tag{1.24}$$

Cancelling $V$ in both parts of the equation and differentiating, we get

$$\frac{dx}{dt} = \frac{k'}{V}(a-x)(b-x) \tag{1.25}$$

If the volume $V$ of the system does not change, it can be introduced into the constant, i.e.

$$\frac{k'}{V} = k \tag{1.26}$$

Equation (1.25) then becomes

$$\frac{dx}{dt} = k(a-x)(b-x) \tag{1.27}$$

Equation (1.27) is a differential equation of the rate of an irreversible second-order reaction. Integration of this equation with account taken of the initial conditions yields

$$k = \frac{1}{t}\frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} \tag{1.28}$$

A glance at Eqs. (1.28) and (1.26) shows that the quantities $k'$ and $k$ have the following dimensions:

$$[k] = T^{-1}M^{-1} \tag{1.29}$$

$$[k'] = T^{-1}M^{-1}L^3 \tag{1.30}$$

where $T$ = time, $M$ = mass and $L$ = length.

TABLE 1.2

**Kinetics of the Reaction of Saponification of Isopropyl Acetate with an Alkali at 25 °C**

$a = 0.022\,70$ mol/dm³ and $b = 0.031\,40$ mol/dm³

| $t$, min | $a-x$ | $b-x$ | $k'$, dm³/mol·min |
|---|---|---|---|
| 0 | 0.01874 | 0.02744 | — |
| 3 | 0.01664 | 0.02534 | 1.49 |
| 4 | 0.01432 | 0.02302 | 1.57 |
| 8 | 0.01092 | 0.01962 | 1.60 |
| 16 | 0.00681 | 0.01551 | 1.70 |
| 20 | 0.00424 | 0.01294 | 1.68 |
| 31 | 0.00245 | 0.01115 | 1.48 |
| 41 | 0.00144 | 0.01014 | 1.23 |
| | | Mean value = 1.54 | |

Table 1.2 gives data characterizing the kinetics of the reaction of saponification of isopropyl acetate with an alkali at 25 °C:

$$CH_3COOCH(CH_3)_2 + NaOH \rightarrow CH_3COONa + (CH_3)_2CHOH$$

If the initial amounts of substances A and B are equal, i.e. $a = b$, then the differential equation of the reaction rate, as can readily be seen, will be written as

$$\frac{dx}{dt} = k(a-x)^2 \tag{1.31}$$

Separating the variables and integrating within the limits from 0 to $t$ and from 0 to $x$, we get

$$k = \frac{1}{t}\frac{x}{a(a-x)} \tag{1.32}$$

When the amount of the reacted substance is equal to half of the initial amount, i.e. when $x = a/2$, the value of $t$ will be equal to $\tau$, i.e. to the half-life. Inserting these values into Eq. (1.32), we get

$$\tau = \frac{1}{ka} \tag{1.33}$$

i.e. the half-life for a second-order reaction is inversely proportional to the amount of initial substance.

Substituting for $k$ in Eq. (1.33) its value from Eq. (1.26) and remembering that $a/V = c_0$, we can write

$$\tau = \frac{1}{k'c_0} \tag{1.34}$$

**1.6. Irreversible Reaction of the $n$-th Order.** The general form of a stoichiometric equation for an $n$-th order reaction is

$$A_1 + A_2 + \ldots + A_n \rightarrow A_1' + A_2' + \ldots + A_n' \tag{1.35}$$

If the reaction proceeds at a constant volume $V$ and with the same number of moles of each of the substances participating in the reaction at the initial moment of time, then the differential equation of the reaction rate will be

$$\frac{dx}{dt} = k(a-x)^n \tag{1.36}$$

where

$$k = \frac{k'}{V^{n-1}} \tag{1.37}$$

It follows from Eq. (1.37) that the quantity $k$ depends on the total volume of the system. Since at a constant temperature the volume of an ideal gas (according to Boyle's law) is inversely proportional to the pressure, the amount of a substance reacting in a unit of time for a reaction in gases is directly proportional to the pressure raised to a power equal to the order of the reaction minus one [see Eq. (1.37)]. Consequently, for first-order reactions the amount of a substance reacting in a unit of time does not depend on the total pressure; for second-order reactions this amount is directly proportional to the total pressure, and for third-order ones—directly proportional to the square of the total pressure, etc.

Separating variables and integrating respectively within the limits from 0 to $t$ and from 0 to $x$, we get

$$k = \frac{1}{t}\frac{1}{n-1}\frac{a^{n-1}-(a-x)^{n-1}}{a^{n-1}(a-x)^{n-1}} \quad (1.38)$$

Inserting into Eq. (1.38) the values $x = a/2$ and $t = \tau$, we get the following expression for the half-life $\tau$:

$$\tau = \frac{1}{k}\frac{1}{n-1}\frac{2^{n-1}-1}{a^{n-1}} \quad (1.39)$$

Thus the half-life is inversely proportional to the amount of the initial substance raised to a power equal to the reaction order minus one. Therefore, by experimentally studying the dependence of the half-life on the amount of the initial substance, we can find the order of a reaction. Taking logarithms of Eq. (1.39), we get

$$\log \tau = \log \frac{2^{n-1}-1}{k(n-1)} - (n-1)\log a \quad (1.40)$$

In the coordinates $\log \tau$ versus $\log a$ this equation describes a straight line (Fig. 1.2). The section cut off by this line on the axis of ordinates is equal to $\log \frac{2^{n-1}-1}{k(n-1)}$, and the tangent of the angle $\varphi$ of inclination of the line ($\tan \varphi = -n + 1$) determines the order of the reaction:

$$n = -\tan \varphi + 1 \quad (1.41)$$

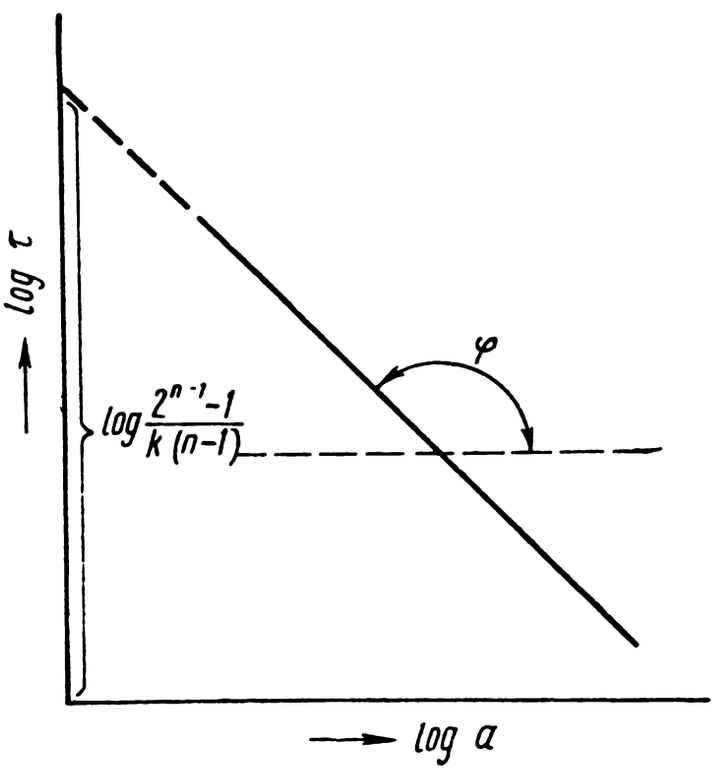


Fig. 1.2. Logarithm of half-life $\tau$ versus logarithm of amount $a$ of initial substance A

The order of a reaction can be found not only from the half-life, but also from the time required for any fraction of the initial substance to react, for example one-fourth, one-third, three-fourths ($\tau_{1/4}$, $\tau_{1/3}$ and $\tau_{3/4}$ respectively), or even from the ratio of the half-life to the time required for the reaction of a definite fraction. Table 1.3 gives expressions for determining the time required for the reaction of a definite fraction of the initial substance in reactions of different orders on condition that the numbers of moles of all the initial substances are the same.

TABLE 1.3

**Time Required for the Reaction of a Definite Fraction of the Initial Substance**

| Reaction order | $\tau_{1/4}$ | $\tau_{1/3}$ | $\tau_{1/2}$ | $\tau_{3/4}$ | $\frac{\tau_{1/2}}{\tau_{1/4}}$ | $\frac{\tau_{1/2}}{\tau_{1/3}}$ | $\frac{\tau_{1/2}}{\tau_{3/4}}$ |
|---|---|---|---|---|---|---|---|
| 1 | $\frac{1}{k}\ln\frac{4}{3}$ | $\frac{1}{k}\ln\frac{3}{2}$ | $\frac{1}{k}\ln 2$ | $\frac{1}{k}\ln 4$ | 2.4 | 1.7 | 0.5 |
| 2 | $\frac{1}{3k'c_0}$ | $\frac{1}{2k'c_0}$ | $\frac{1}{k'c_0}$ | $\frac{3}{k'c_0}$ | 3 | 2 | 0.33 |
| 3 | $\frac{7}{18k'c_0^2}$ | $\frac{5}{8k'c_0^2}$ | $\frac{3}{2k'c_0^2}$ | $\frac{15}{2k'c_0^2}$ | 3.86 | 2.4 | 0.20 |
| $n$ | $\frac{\left(\frac{4}{3}\right)^{n-1}-1}{(n-1)\,k'c_0^{n-1}}$ | $\frac{\left(\frac{3}{2}\right)^{n-1}-1}{(n-1)\,k'c_0^{n-1}}$ | $\frac{2^{n-1}-1}{(n-1)\,k'c_0^{n-1}}$ | $\frac{4^{n-1}-1}{(n-1)\,k'c_0^{n-1}}$ | $\frac{2^{n-1}-1}{\left(\frac{4}{3}\right)^{n-1}-1}$ | $\frac{2^{n-1}-1}{\left(\frac{3}{2}\right)^{n-1}-1}$ | $\frac{2^{n-1}-1}{4^{n-1}-1}$ |

**1.7. Reversible Reaction of the First Order.** The reactions of the mutual conversion of isomers, for example *d*-menthone $\rightleftarrows$ *l*-menthone or ammonium thiocyanate $\rightleftarrows$ thiocarbamide [$NH_4NCS \rightleftarrows (NH_2)_2CS$] can serve as examples of reversible reactions.

The general form of the stoichiometric equation of a first-order reversible reaction is

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

The reaction simultaneously proceeds in two opposite directions and therefore its rate is equal to the difference between the rates of the forward and reverse reactions, each of which is a first-order one, i.e.

$$-\frac{d(a-x)}{dt} = k_1(a-x) - k_2(b+x) \tag{1.42}$$

where $a$ and $b$ = initial amount respectively of substance A and B, mole

$x$ = amount of substance A that has reacted by the time $t$, mole.

This follows from the *principle of independence* (principle of coexistence) of the forward and reverse reactions. According to this principle, *if several reactions proceed simultaneously in a system, each of them is independent of the others and its rate is directly proportional to the concentrations of the reactants.* A finite change in the concentration of a given substance is the result of all these independent changes. This principle has been verified experimentally. It was found that experimental data and results of calculations according to theoretical equations coincide quite well for reversible, concurrent (parallel) and consecutive reactions.

Differentiation of Eq. (1.42) gives

$$\frac{dx}{dt} = k_1(a-x) - k_2(b+x) \tag{1.43}$$

After transformation, Eq. (1.43) becomes

$$\frac{dx}{dt} = (k_1+k_2)\left(\frac{k_1a-k_2b}{k_1+k_2} - x\right) \tag{1.44}$$

Let

$$\frac{k_1a-k_2b}{k_1+k_2} = L \tag{1.45}$$

Equation (1.44) thus becomes

$$\frac{dx}{dt} = (k_1+k_2)(L-x) \tag{1.46}$$

Separating variables, we get

$$\frac{dx}{L-x} = (k_1+k_2)\,dt \tag{1.47}$$

Integration of this equation within the limits, respectively, from 0 to $x$ and from 0 to $t$ and solution with respect to $k_1 + k_2$ yield

$$k_1 + k_2 = \frac{1}{t} \ln \frac{L}{L - x} \tag{1.48}$$

Consequently, to find the sum of the rate constants for the forward and reverse reactions it is necessary to know the value of $L$, which can be determined by dividing the numerator and denominator in Eq. (1.45) by $k_2$ and taking into account that

$$\frac{k_1}{k_2} = K \tag{1.49}$$

where $K$ is the equilibrium constant (see Vol. 1, Secs. 8.2 and 8.7), i.e.

$$\frac{Ka - b}{1 + K} = L \tag{1.50}$$

To find the value of $L$ it is therefore necessary to know the equilibrium constant of the given reaction.

The rates of the forward and reverse reactions at the moment of equilibrium are the same, hence

$$\frac{dx}{dt} = 0 \tag{1.51}$$

Inserting Eq. (1.51) into Eq. (1.43) and designating the amount of substance A that has reacted by the moment of equilibrium by the subscript $\infty$, we get

$$k_1 (a - x_\infty) - k_2 (b + x_\infty) = 0 \tag{1.52}$$

Hence

$$K = \frac{k_1}{k_2} = \frac{b + x_\infty}{a - x_\infty} \tag{1.53}$$

Knowing the numerical value of $L$, we can use Eq. (1.48) to compute the sum of the rate constants $k_1 + k_2$, and, in addition, knowing the numerical value of the equilibrium constant and taking into account that it is equal to the ratio between the rate constants of the forward and reverse reactions, we can find each rate constant separately.

It is sometimes formally convenient to consider a first-order reversible reaction as an irreversible one. For this purpose it can be assumed that $x_\infty$ of the initial substance has reacted by the end of the reaction. The differential equation of the reaction rate will thus become

$$\frac{dx}{dt} = k (x_\infty - x) \tag{1.54}$$

Separating variables and integrating respectively within the limits from 0 to $x$ and from 0 to $t$, we get

$$k = \frac{1}{t} \ln \frac{x_\infty}{x_\infty - x} \tag{1.55}$$

TABLE 1.4

**Kinetics of Reaction of Isomerization of β-Hydroxy-Crotonic Ester into Acetoacetic Ester at 25 °C**

$a=1$ mole and $x_\infty=0.922$ mole

| $t$, h | $1-x$, mol | $x_\infty-x$, mol | $k\times10^4$, $h^{-1}$ | $t$, h | $1-x$, mol | $x_\infty-x$, mol | $k\times10^4$, $h^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.366 | 0.288 | — | 333.3 | 0.130 | 0.052 | 47 |
| 71.8 | 0.277 | 0.199 | 47 | 383.5 | 0.121 | 0.043 | 46 |
| 145.5 | 0.215 | 0.137 | 47 | 478.3 | 0.106 | 0.028 | 45 |
| 215.8 | 0.174 | 0.096 | 47 | 506.0 | 0.100 | 0.022 | 47 |
| 264.3 | 0.152 | 0.074 | 47 | | | | |

It follows from Eqs. (1.46) and (1.54) that

$$L = x_\infty \tag{1.56}$$

and

$$k = k_1 + k_2 \tag{1.57}$$

Table 1.4 contains data on the kinetics of the reaction of isomerization of β-hydroxy-crotonic ester into acetoacetic ester

$$CH_3-\underset{\underset{OH}{|}}{C}=CH-COOC_2H_5 \rightleftarrows CH_3-CO-CH_2-COOC_2H_5$$

proceeding at 25 °C.

The table confirms the principle of independence of simultaneously proceeding reactions.

**1.8. Reversible Reaction of the Second Order.** A typical example of such a reaction is the reaction of hydrolysis of an ester or the reverse reaction of esterification

$$CH_3COOC_2H_5+H_2O \rightleftarrows CH_3COOH+C_2H_5OH$$

This reaction can be written in the general form as

$$A+B \rightleftarrows C+D$$

As in the previous case, the rate of the reaction will be equal to the difference between the rates of the forward and reverse reactions, i.e.

$$-\frac{d(a-x)}{V\,dt} = k_1' c_A c_B - k_2' c_C c_D \tag{1.58}$$

where $a$ = initial number of moles of substance A

$x$ = number of moles of substance A that have reacted by the time $t$

$k_1'$ and $k_2'$ = rate constants of forward and reverse reactions

$c_i$ = concentration of a reactant or product by the time $t$.

Differentiation yields

$$\frac{dx}{V\,dt} = k_1' c_A c_B - k_2' c_C c_D \tag{1.59}$$

Let us consider the simplest case when the numbers of moles of the reactants at the initial moment $t = 0$ are the same and are equal to the quantity $a$, and the numbers of moles of the products are equal to zero. Equation (1.59) will now become

$$\frac{dx}{V\,dt} = k_1' \frac{(a-x)^2}{V^2} - k_2' \frac{x^2}{V^2} \tag{1.60}$$

Cancelling $V$ in both parts of the equation, we get

$$\frac{dx}{dt} = k_1 (a-x)^2 - k_2' x^2 \tag{1.61}$$

where

$$k_1 = \frac{k_1'}{V} \quad \text{and} \quad k_2 = \frac{k_2'}{V}$$

Algebraic transformations yield

$$\frac{dx}{dt} = (k_1 - k_2) \left\{ x^2 - 2\frac{k_1 a}{k_1 - k_2} x + \frac{k_1 a^2}{k_1 - k_2} \right\} \tag{1.62}$$

The expression in braces can be represented as the product of two binomials. Hence

$$\frac{dx}{dt} = (k_1 - k_2)(m_1 - x)(m_2 - x) \tag{1.63}$$

where $m_1$ and $m_2$ are the roots of a quadratic equation that can be written as follows:

$$x^2 - \frac{2aK}{K-1} x + \frac{a^2 K}{K-1} = 0 \tag{1.64}$$

where $K = k_1/k_2$ is the equilibrium constant.

The roots of Eq. (1.64) are equal to

$$m_{1,2} = \frac{a(K \pm \sqrt{K})}{K-1} \tag{1.65}$$

Separating the variables in Eq. (1.63) and integrating it, we get

$$k_1 - k_2 = \frac{1}{t} \frac{1}{m_1 - m_2} \ln \frac{m_2 (m_1 - x)}{m_1 (m_2 - x)} \tag{1.66}$$

Knowing the equilibrium constant $K$, we can find the respective rate constants $k_1$ and $k_2$ for the forward and reverse reactions.

**1.9. Concurrent Reactions.** The reactants sometimes react simultaneously in several directions. For example, in the nitration of phenol three isomers are formed: *o*-, *m*- and *n*-nitrophenol; upon the heating of Berthollet's salt two reactions proceed simultaneously

$$6KClO_3 - \begin{cases} \longrightarrow 2KCl + 3O_2 \\ \longrightarrow 3KClO_4 + KCl \end{cases}$$

Such reactions are called *concurrent* (or *parallel*). Let us consider the simplest case of two concurrent irreversible monomolecular reactions

$$A \rightarrow B \text{ and } A \rightarrow C$$

The rate of the first reaction is

$$\frac{dx_1}{dt} = k_1 (a - x) \tag{1.67}$$

and of the second

$$\frac{dx_2}{dt} = k_2 (a - x) \tag{1.68}$$

where $x_1$ and $x_2$ = number of moles of substances B and C formed by the time $t$, respectively

$x = x_1 + x_2$ = total number of moles of substance A that have reacted by the time $t$

$k_1$ and $k_2$ = rate constants of first and second reactions.

The rate of reaction of substance A in both directions will be equal to the sum of the rates of reaction in each of the directions, i.e.

$$\frac{dx_1}{dt} + \frac{dx_2}{dt} = \frac{dx}{dt} \tag{1.69}$$

Using Eqs. (1.67), (1.68) and (1.69), we get

$$\frac{dx}{dt} = k_1 (a - x) + k_2 (a - x) \tag{1.70}$$

or

$$\frac{dx}{dt} = (k_1 + k_2)(a - x) \tag{1.71}$$

Integration of this equation yields

$$k_1 + k_2 = \frac{1}{t} \ln \frac{a}{a - x} \tag{1.72}$$

This equation differs from the similar equation (1.12) for a first-order reaction in that it contains the sum of the rate constants of both concurrent reactions. For three concurrent first-order reactions the left-hand part of the equation will contain the sum of three constants.

For two concurrent irreversible second-order reactions we get

$$\frac{dx}{dt} = (k_1 + k_2)(a - x)(b - x) \tag{1.73}$$

Integration of this equation yields

$$k_1 + k_2 = \frac{1}{(a - b)\, t} \ln \frac{b(a - x)}{a(b - x)} \tag{1.74}$$

Equations (1.72) and (1.74) make it possible to determine the sum of the rate constants. If it is necessary to find each constant separately, we must have another equation containing these constants. We shall show how such an equation is obtained for the example of two concurrent irreversible reactions of the first order. Dividing Eq. (1.67) by Eq. (1.68), we get

$$\frac{dx_1}{dx_2} = \frac{k_1}{k_2} \tag{1.75}$$

Integration of this equation within the limits, respectively, from 0 to $x_1$ and 0 to $x_2$ yields

$$\frac{x_1}{x_2} = \frac{k_1}{k_2} \tag{1.76}$$

After determining at a certain moment of time the amounts of substances B and C equal to $x_1$ and $x_2$, we get the ratio of the rate constants of both parallel reactions and, consequently, solution of the simultaneous equations (1.76) and (1.72) allows us to compute each constant separately.

**1.10. Consecutive Reactions.** *Consecutive* reactions are ones with *intermediate steps* or *stages*. Many examples of such reactions can be given. Most reactions proceed via intermediate stages. True, it is not always possible to establish the nature of the intermediates owing to experimental difficulties. Consecutive reactions include, in particular, the reactions of saponification of esters of dibasic acids with an alkali, for example ethyl succinate with sodium hydroxide

$$C_2H_4(COOC_2H_5)_2 + H_2O + 2NaOH \longrightarrow C_2H_4 \begin{cases} COOC_2H_5 \\ COONa \end{cases} +$$

$$+ C_2H_5OH + NaOH \longrightarrow C_2H_4(COONa)_2 + 2C_2H_5OH$$

or the hydrolysis of a hydroxy acid ester in the presence of acids with the following formation of lactone, for example

$$CH_2(OH)CH_2COOC_2H_5 \longrightarrow CH_2(OH)CH_2COOH + C_2H_5OH$$

$$\downarrow$$

$$\underbrace{CH_2CH_2CO}_{O} + H_2O$$

The reaction of thermal cracking of hydrocarbons should also be considered as a consecutive one. It proceeds with the consecutive transformation of high-molecular hydrocarbons into low-molecular ones. The latter at high temperatures transform into gaseous hydrocarbons (methane, ethane) and into high-molecular hydrocarbons with a low hydrogen content, called "coke".

Let us first consider a very simple case of two consecutive monomolecular reactions, i.e. when one mole of substance A yields one mole of subtance B, and the latter yields one mole of substance C.

Assume that at the initial moment of time $t = 0$ we have $a$ moles of substance A, and by the moment of time $t$ there remain $a - x$ moles of substance A, and there appear $x - y$ moles of substance B and $y$ moles of substance C.

Using Eq. (1.8a), we can write

$$\frac{dx}{dt} = k_1 (a - x) \tag{1.77}$$

Integration of this equation yields

$$a - x = ae^{-k_1 t} \tag{1.78}$$

The rate of reaction of intermediate B

$$\frac{d(x-y)}{dt} = k_1 (a - x) - k_2 (x - y) \tag{1.79}$$

Inserting Eq. (1.78) into Eq. (1.79), we get

$$\frac{d(x-y)}{dt} = k_1 a e^{-k_1 t} - k_2 (x - y) \tag{1.80}$$

or

$$\frac{d(x-y)}{dt} + k_2 (x - y) = k_1 a e^{-k_1 t} \tag{1.81}$$

Solution of differential equation (1.81) gives

$$x - y = a \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \tag{1.82}$$

$$y = a \left( 1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right) \tag{1.83}$$

The course of the solution is considered in detail below.

Let $x - y = z$. Equation (1.81) therefore becomes

$$\frac{dz}{dt} + k_2 z = k_1 a e^{-k_1 t} \tag{1.84}$$

Equating the left-hand part of this equation to zero, we get

$$\frac{dz}{dt} + k_2 z = 0 \tag{1.85}$$

Separating variables and integrating the resulting expression, we get

$$\ln z = -k_2 t + \ln E \tag{1.86}$$

or

$$z = Ee^{-k_2 t} \tag{1.86a}$$

where $E$ is a constant obtained in integrating Eq. (1.85).

Since the right-hand part of Eq. (1.84) contains a function of $t$, and not zero, we shall also consider the quantity $E$ in Eq. (1.86a) as a function of time. Differentiation of Eq. (1.86a) with respect to $t$ gives

$$\frac{dz}{dt} = -k_2 E e^{-k_2 t} + e^{-k_2 t} \frac{dE}{dt} \tag{1.87}$$

Inserting Eqs. (1.86a) and (1.87) into Eq. (1.84), we obtain

$$-k_2 E e^{-k_2 t} + e^{-k_2 t} \frac{dE}{dt} + k_2 E e^{-k_2 t} = k_1 a e^{-k_1 t} \tag{1.88}$$

or

$$\frac{dE}{dt} = \frac{k_1 a e^{-k_1 t}}{e^{-k_2 t}} \tag{1.89}$$

or

$$dE = k_1 a e^{(k_2 - k_1) t} dt \tag{1.90}$$

whence (after integration)

$$E = \frac{k_1}{k_2 - k_1} a e^{(k_2 - k_1) t} + C \tag{1.91}$$

Let us insert Eq. (1.91) into Eq. (1.86a), whence

$$z = \frac{k_1}{k_2 - k_1} a e^{(k_2 - k_1) t} e^{-k_2 t} + C e^{-k_2 t} \tag{1.92}$$

or

$$z = \frac{k_1}{k_2 - k_1} a e^{-k_1 t} + C e^{-k_2 t} \tag{1.93}$$

But when $t = 0$, the quantity $z$ is also equal to zero. Hence

$$C = -\frac{k_1}{k_2 - k_1} a \tag{1.94}$$

Inserting Eq. (1.94) into Eq. (1.93) and returning to the previous symbols, we get

$$x - y = a \left( \frac{k_1}{k_2 - k_1} e^{-k_1 t} - \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right) \tag{1.95}$$

or

$$x - y = a \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \tag{1.96}$$

Let us substitute for $x$ in Eq. (1.96) its value from Eq. (1.78). Hence

$$y = a (1 - e^{-k_1 t}) - a \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \tag{1.97}$$

or

$$y = a \left( 1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right) \tag{1.98}$$

Figure 1.3 shows curves corresponding to Eqs. (1.82), (1.78) and (1.83). The curve $(x - y)$ showing the change in the amount of intermediate B with time has a maximum at $t_{max}$, at which the greatest amount of B forms. We find the value of $t_{max}$ from the condition of

an extreme

$$\frac{d(x-y)}{dt}=0 \tag{1.99}$$

Differentiation of Eq. (1.82) gives

$$\frac{d(x-y)}{dt}=a\frac{k_1}{k_2-k_1}(-k_1e^{-k_1t}+k_2e^{-k_2t}) \tag{1.100}$$

Equating the derivative to zero, we have

$$k_1e^{-k_1t_{\max}}=k_2e^{-k_2t_{\max}} \tag{1.101}$$

After taking logarithms, we get

$$t_{\max}=\frac{\ln k_1-\ln k_2}{k_1-k_2} \tag{1.102}$$

Let

$$k_2/k_1=r, \text{ i.e. } k_2=k_1r \tag{1.103}$$

Insertion of Eq. (1.103) into Eq. (1.102) gives

$$t_{\max}=\frac{\ln r}{(r-1)k_1} \tag{1.104}$$

After the introduction of this value of $t_{\max}$ into Eq. (1.82), the latter becomes

$$(x-y)_{\max}=\frac{a}{1-r}\left(e^{-r\frac{\ln r}{r-1}}-e^{-\frac{\ln r}{r-1}}\right) \tag{1.105}$$

The maximum amount of intermediate B depends not on the absolute values of the rates of both reactions, but only on the ratio of these rates. The greater the value of $k_2/k_1$, the greater is the ordinate of the maximum of the curve $x-y=f(t)$ (see Fig. 1.3) and the closer is this maximum to the beginning of the reaction.

The curve $y=f_1(t)$ characterizing the accumulation of the product C with time has a point of inflection. The latter coincides with the maximum point on the curve $x-y=f(t)$. The point of inflection on the curve $y=f_1(t)$ indicates that substance C is formed with an initial acceleration. Calculations show that at low values of the ratio $k_1/k_2$, the curve of $y$ first practically coincides with the axis of abscissas, i.e. substance C during a certain interval of time after the beginning of the reaction cannot be detected analytically. This interval of time is called the *period of induction*.

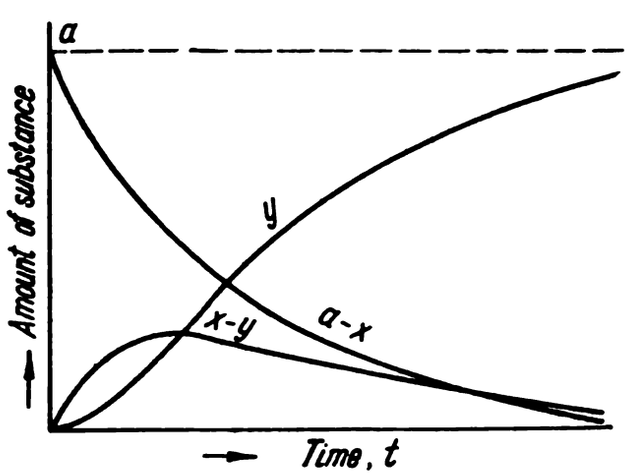


Fig. 1.3. Change in amount of reactants with time for a first-order consecutive reaction ($k_1=2k_2$)

If $k_1 < k_2$, then in a sufficiently great interval of time

$$e^{-k_2 t} \ll e^{-k_1 t}$$

Consequently, the second addend in parentheses in Eq. (1.82) may be discarded. Therefore

$$x - y = \frac{ak_1}{k_2 - k_1} e^{-k_1 t} \tag{1.106}$$

Since $ae^{-k_1 t} = a - x$, then

$$x - y = \frac{(a - x) k_1}{k_2 - k_1} \tag{1.107}$$

or

$$\frac{x - y}{a - x} = \frac{k_1}{k_2 - k_1} \tag{1.108}$$

i.e. the ratio of the amounts of substances B and A in a definite interval of time after the beginning of a reaction becomes constant and does not practically change during a certain interval. In other words, the amounts of substances A and B diminish to the same extent. Such a state is called *transient* equilibrium.

If $k_1 \ll k_2$, then

$$\frac{x - y}{a - x} = \frac{k_1}{k_2} = \frac{\tau_2}{\tau_1} \tag{1.109}$$

where $\tau_2$ and $\tau_1$ are the half-lives of substances B and A.

Equilibrium corresponding to Eq. (1.109) is called *secular* equilibrium.

In addition, when $k_1 \ll k_2$ Eq. (1.83) becomes

$$y = a(1 - e^{-k_1 t}) \tag{1.110}$$

since we may neglect the third addend in the parentheses and the value of $k_1$ in the denominator of the second addend. Therefore such a reaction proceeds as a first-order one. Only at the very beginning of the reaction does its rate deviate from that described by the equation for a simple monomolecular reaction.

Experience shows that the kinetics of such reactions can be described by an equation for a first-order reaction if w do not take into consideration the initial period of the reaction. This is explained by the fact that the majority of reactions belong to consecutive ones in which the final stage proceeds much more rapidly than the intermediate ones.

For the more complicated process

$$A \rightarrow B \rightarrow C \rightarrow D$$

another equation is added for the rate of reaction of intermediate C:

$$\frac{d(y-z)}{dt} = k_2(x-y) - k_3(y-z) \tag{1.111}$$

where $y - z$ is the number of moles of C at the time $t$.

Substituting for $(x - y)$ its value from Eq. (1.82), we get

$$\frac{d(y-z)}{dt} + k_3(y-z) = a\frac{k_1k_2}{k_2-k_1}(e^{-k_1t} - e^{-k_2t}) \tag{1.112}$$

Integration of this equation yields

$$y - z = a(C_1e^{-k_1t} + C_2e^{-k_2t} + C_3e^{-k_3t}) \tag{1.113}$$

where

$$C_1 = \frac{k_1k_2}{(k_2-k_1)(k_3-k_1)}$$

$$C_2 = \frac{k_1k_2}{(k_1-k_2)(k_3-k_2)}$$

$$C_3 = \frac{k_1k_2}{(k_1-k_3)(k_2-k_3)}$$

The problem is solved in just as simple a way with a greater number of reaction stages. For higher order reactions it is not always possible to integrate the equations obtained.

**1.11. Methods for Determining the Order of a Reaction.** To determine the order of a reaction as a whole, it is first necessary to establish the order with respect to each substance entering into the reaction. The sum of these reaction orders will give the order of the overall reaction. To find the order of a reaction with respect to a given substance, such conditions must be created in which the concentration of only the given substance will change in the course of the reaction. For this purpose the concentrations of all the remaining substances participating in the reaction must be so great that their change in time may be neglected. Consequently, the values of these concentrations may be introduced into the rate constant. Hence for the reaction

$$\nu_1A + \nu_2B + \nu_3C \rightarrow \nu_4D + \nu_5E$$

proceeding at a constant volume we can write

$$-\frac{\partial c_A}{\partial t} = k_1c_A^{n_i} \tag{1.114}$$

where $k_1 = kc_B^{n_2}c_C^{n_3}$

$n_i$ = exponent which the concentration of the $i$-th substance has in the equation of the reaction, determining the reaction order with respect to this substance.

The reaction order with respect to a given substance can be determined according to its half-life. For this purpose it is necessary to

conduct several experiments, each time setting the initial concentration of the given substance, and establish how the half-life depends on the amount of the initial substance. As already indicated in Sec. 1.6, the half-life is inversely proportional to the amount or concentration of the initial substance raised to a power equal to the reaction order minus one. Conducting experiments with each substance separately, we can determine $n_1$, $n_2$, etc. The summary reaction order ($n$) will be

$$n = n_1 + n_2 + \ldots + n_i \tag{1.115}$$

This method is especially convenient for determining the order of reactions between gaseous substances.

The reaction order can also be determined as follows. When conducting a given reaction, all the substances except one, say A, are taken in excess. The reaction is repeated twice, setting different initial values of the concentration. We can thus write two rate equations

$$-\frac{\partial c'_A}{\partial t} = k_1 c'^{n_1}_A \tag{1.116}$$

and

$$-\frac{\partial c''_A}{\partial t} = k_1 c''^{n_1}_A \tag{1.117}$$

Dividing Eq. (1.117) by Eq. (1.116), we get

$$\frac{\partial c'_A/\partial t}{\partial c''_A/\partial t} = \left(\frac{c'_A}{c''_A}\right)^{n_1} \tag{1.118}$$

Taking logarithms and solving the equation with respect to $n_1$, we get

$$n_1 = \frac{\log(\partial c'_A/\partial t) - \log(\partial c''_A/\partial t)}{\log c'_A - \log c''_A} \tag{1.119}$$

The differentials may be replaced by finite increments, and we thus have

$$n_1 = \frac{\log(\Delta c'_A/\Delta t) - \log(\Delta c''_A/\Delta t)}{\log c'_A - \log c''_A} \tag{1.120}$$

It is Eq. (1.120) that makes it possible to determine the order of the reaction with respect to substance A. For this purpose it is necessary to find the change in the concentrations $\Delta c'_A$ and $\Delta c''_A$ during the time $\Delta t$, with a view to the fact that two different values of the initial concentration of substance A are taken. The concentrations of all the remaining substances are selected very great to be able to neglect their change during the time $\Delta t$. The mean values of $c'_A$ and $c''_A$ for the given interval of time should be taken in the denominator. The same procedure should be followed in determining the order of the reaction with respect to substances B and C. Summation of the elementary reaction orders gives the order of the overall reaction.

It is not at all necessary to start the reaction both times from the beginning. In determining the concentration of a given substance at any moment of time, one of these moments may be taken as the zero one, the concentration of the substance at this moment as the initial one, and the concentration after the time $\Delta t$ as the final one for the given period of time.

The order of a reaction with respect to each product can be determined from Eq. (1.114) graphically (Fig. 1.4). Plotting $\log(-\Delta c_A/\Delta t)$ versus $\log c_A$, we obtain a straight line, the tangent of whose angle of inclination is numerically equal to the order of the reaction with respect to the given substance. To plot such a curve, it is necessary to experimentally determine the mean rate of the reaction $(-\Delta c_A/\Delta t)$ and the concentration of substance A at each moment of time. The value of $(-\Delta c_A/\Delta t)$ will correspond to the time at the middle of the interval $\Delta t$, if the latter is sufficiently small.

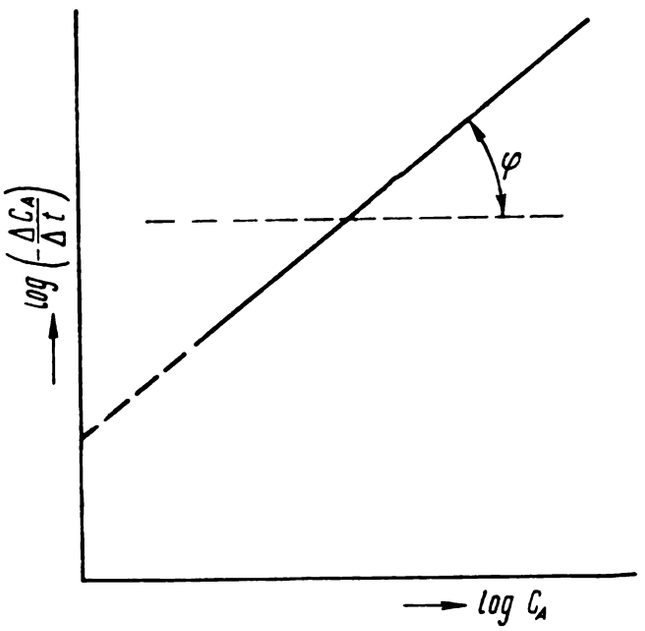


Fig. 1.4. Graphical determination of reaction order with respect to given substance

**1.12. Influence of Temperature on Reaction Rate.** In the general case the rate of a chemical reaction grows with an increase in the temperature. Experience shows that the rate of a reaction grows from two to four times when the temperature increases by 10 K. To characterize the temperature dependence of the rate of a chemical reaction, the *temperature coefficient of the reaction rate* $\gamma$ was introduced. It is the ratio of the rate constant of a chemical reaction at the temperature $T+10$ to the rate constant at the temperature $T$, i.e

$$\gamma = \frac{k_{T+10}}{k_T} \tag{1.121}$$

The average value of this coefficient is three. Consequently, when the temperature changes by 100 K the rate of a reaction changes $3^{10} = 59\,049$ times. The temperature coefficient of the reaction rate allows us to calculate the rate constants at different temperatures.

Taking logarithms in Eq. (1.121), we get

$$\log k_{T+10} - \log k_T = \log \gamma \tag{1.122}$$

Designating $\log k_{T+10} - \log k_T$ by $\Delta \log k$ and dividing both parts of this equation by $\Delta T = 10$ K, we get

$$\frac{\Delta \log k}{\Delta T} = \frac{\log \gamma}{10} \tag{1.123}$$

If we assume that within the limits of 10 K the temperature coefficient remains constant, Eq. (1.123) can be written as

$$\frac{d \log k}{dT} = \frac{\log \gamma}{10} \tag{1.124}$$

Integration of Eq. (1.124) yields

$$\log \frac{k_{T_2}}{k_{T_1}} = \frac{\log \bar{\gamma}}{10}(T_2 - T_1) \tag{1.125}$$

where $\bar{\gamma}$ is the mean temperature coefficient within the temperature interval $T_2 - T_1$.

The appraisal of the temperature dependence of the rate of a chemical reaction given above has a very approximate nature and a low practical value. A more substantiated dependence can be obtained with the aid of an equation for the isochore or isobar of a chemical reaction. Without the subscripts characterizing the conditions in which the process proceeds, the equations for an isochore and isobar are written in the same form, namely,

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{1.126}$$

where $K = k_1/k_2$ = chemical equilibrium constant
$k_1$ and $k_2$ = rate constants of forward and reverse reactions
$\Delta H$ = heat of chemical reaction
$R$ = universal gas constant
$T$ = absolute temperature.

Substituting for the equilibrium constant the ratio of the rate constants, we get

$$\frac{d \ln \frac{k_1}{k_2}}{dT} = \frac{d \ln k_1 - d \ln k_2}{dT} = \frac{\Delta H}{RT^2} \tag{1.127}$$

Writing the heat of a chemical reaction as the difference of two quantities

$$\Delta H = E_1 - E_2$$

we can rewrite Eq. (1.127) as follows:

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_2}{dT} = \frac{E_1}{RT^2} - \frac{E_2}{RT^2} \tag{1.128}$$

It can be considered with an accuracy to the constant $B$ that the addends of the right-hand and left-hand parts are equal to one another in pairs, i.e.

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} + B \tag{1.129}$$

$$\frac{d \ln k_2}{dT} = \frac{E_2}{RT^2} + B \tag{1.130}$$

Experience shows that $B = 0$. Therefore, discarding the subscripts, we can write Eqs. (1.129) and (1.130) as follows:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \tag{1.131}$$

This equation, called the *Arrhenius equation*, characterizes the dependence of the rate constant of a chemical reaction $k$ on the temperature $T$. The quantity $E$ has the dimension of energy and is known as the *activation energy*. The latter can be defined as the excess energy in comparison with the mean energy of molecules at a given temperature which a molecule must have to enter into a chemical reaction.

It is easy to integrate Eq. (1.131). Assuming $E$ to be a constant quantity, we get

$$\ln k = -\frac{E}{RT} + \ln C \tag{1.132}$$

where $\ln C$ is an integration constant.

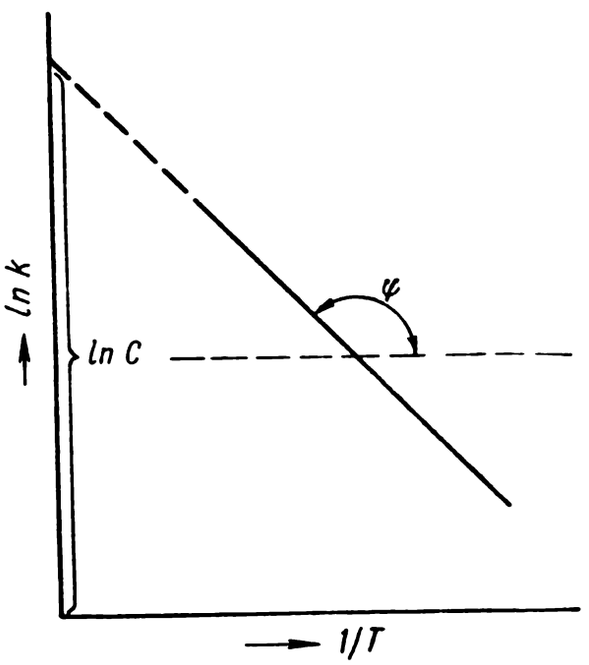


Fig. 1.5. Logarithm of rate constant of chemical reaction versus inverse temperature

If we plot this relation in the coordinates $\ln k$ versus $1/T$ (Fig. 1.5), we get a straight line. The section cut off by this line on the axis of ordinates at $1/T = 0$ is equal to $\ln C$, and the tangent of the angle of inclination of the line

$$\tan \varphi = -\frac{E}{R} \tag{1.133}$$

Hence we can determine the energy of activation of a chemical reaction.

Involution of Eq. (1.132) gives

$$k = Ce^{-E/RT} \tag{1.134}$$

A glance at this equation shows that the preexponential factor $C$ and the activation energy $E$ are the constants characterizing a reaction. The higher the value of $E$, the lower (at a given value of $C$) is the rate of a chemical reaction.

Figure 1.6 shows the logarithm of the rate constant versus the inverse absolute temperature for the reaction of decyclization of cyclopropane. This reaction proceeds according to an equation of the first-order reaction. Its activation energy is 65 kcal/mol, and $\log C = 15.3$.

The temperature dependence of the rate of this reaction can be expressed by the equation

$$k = 2 \times 10^{15} e^{-65\,000/RT}$$

If we integrate Eq. (1.131) within the limits from $T_1$ to $T_2$, we get

$$\ln \frac{k_2}{k_1} = \frac{E}{R} \frac{T_2 - T_1}{T_1 T_2} \qquad (1.135)$$

where $k_2$ = rate constant of chemical reaction at temperature $T_2$
$k_1$ = ditto at temperature $T_1$.

Thus, knowing the value of $k_1$ at any temperature $T_1$, we can compute the value of $k_2$ at the temperature $T_2$.

The relation between the activation energy and the heat of a reaction can be illustrated with the aid of the notion of the *energy barrier*. A chemical reaction can be considered as the transition of a system from energy state I to energy state II accompanied by the heat $\Delta H$. It can be seen from Fig. 1.7 that a transition from state I to state II is possible with the expenditure of the energy $E_1$. A reverse transition is possible with the expenditure of the energy $E_2$. When the reaction is conducted in the forward direction, the amount of energy liberated is

$$-\Delta H = E_2 - E_1 \qquad (1.136)$$

The quantity $-\Delta H$ is equal (according to Hess's law) to the difference between the enthalpies of the reactants and products:

$$-\Delta H = H_1 - H_2 \qquad (1.137)$$

counted from a certain initial value taken as zero ($H = 0$).

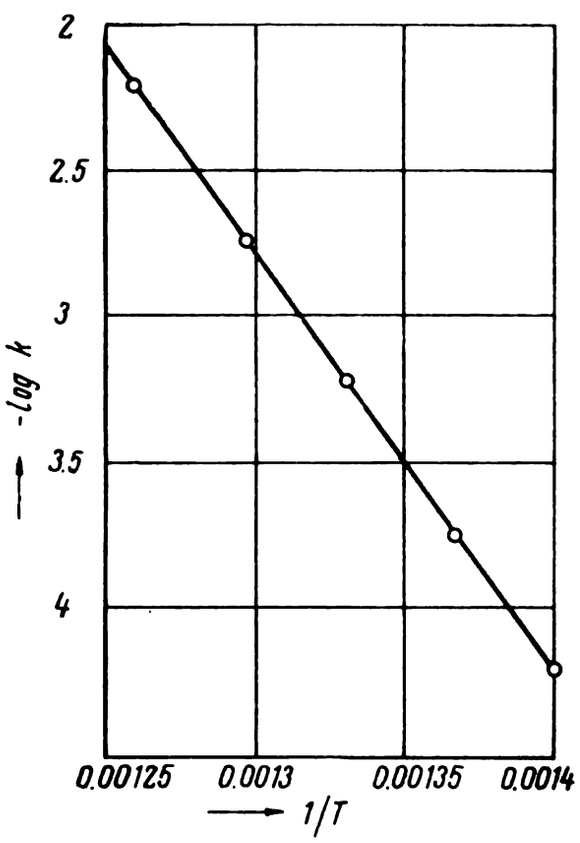


Fig. 1.6. Logarithm of rate constant versus inverse temperature for reaction of decyclization of cyclopropane

**1.13*. Thermal Explosion.** If an exothermic reaction proceeds in a closed volume, then in the particular case of a reaction of combustion, processes are possible when the heat liberated into the surroundings is less than the heat of the reaction. This leads to self-heating of the reaction mixture and, consequently, to an increase in the rate of the reaction. The phenomenon of the transition of a reaction to non-stationary progressively accelerating burning out of a mixture is called a *thermal explosion*.

Suppose we have a closed vessel filled with a combustible mixture. Let the temperature of the mixture be $T_0$ and its concentration $c$. The heat of the reaction is transmitted to the walls of the vessel, and from them to the surroundings. Let the temperature of the latter at the beginning of the process also be equal to

$T_0$. The nature of the heat processes accompanying the combustion of the mixture can easily be depicted graphically if we lay off the temperature along the axis of abscissas and the quantity of heat liberated and removed from the vessel

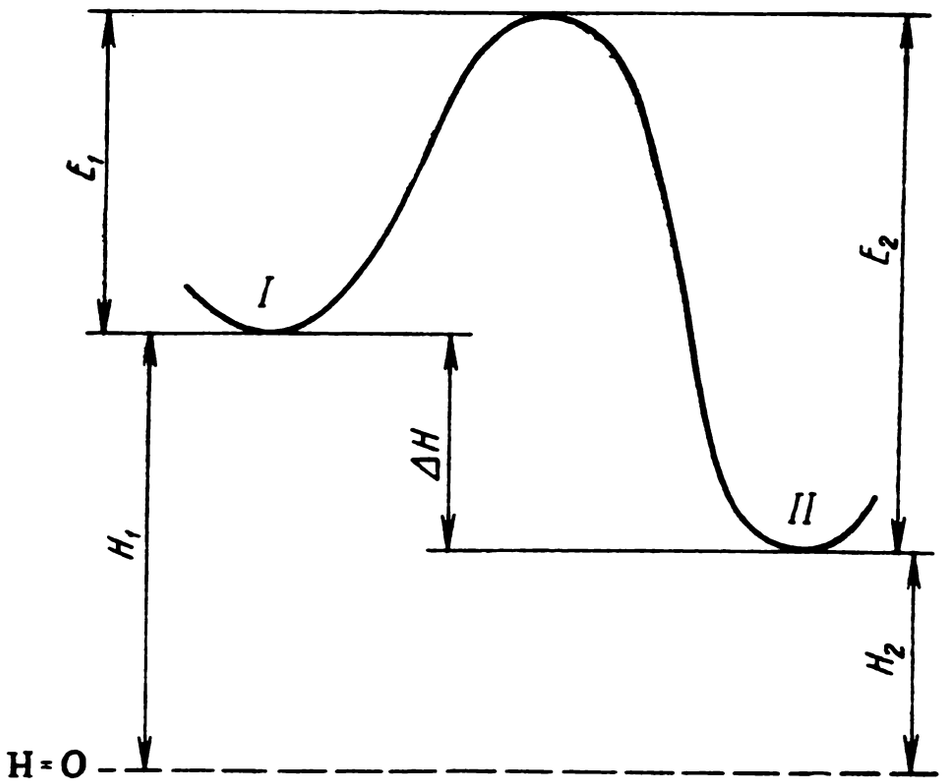


Fig. 1.7. Energy changes in the process of a chemical reaction

in a unit of time along the axis of ordinates (Fig. 1.8). Curve *a* characterizes the temperature dependence of the heat of the chemical reaction liberated in a unit of time in adiabatic conditions (the temperature rises owing to adiabatic liberation of the heat of reaction). Curve *b* shows the temperature dependence of the quantity of heat removed. The heat removal curve always has a smaller curvature than the heat liberation one, and with a sufficient degree of accuracy (within a small interval of temperatures) it can be assumed to be a straight line. In a stationary state the quantities of heat liberated and removed in a unit of time should be equal. A glance at Fig. 1.8 shows that there may be two such stationary states (points *A* and *C*), one (point *B* on curve *b'*) or zero (curve *b"*). The number of stationary states depends on the initial temperature $T_0$. If the initial temperature is raised, we can transfer curve *b* parallel to itself to position *b'* or *b"*. If two stationary states of the system are possible, only one of them, namely *A*, will correspond to stable equilibrium. Indeed, below point *A* the quantity of heat liberated in a unit of time as a result of the reaction will be greater than the

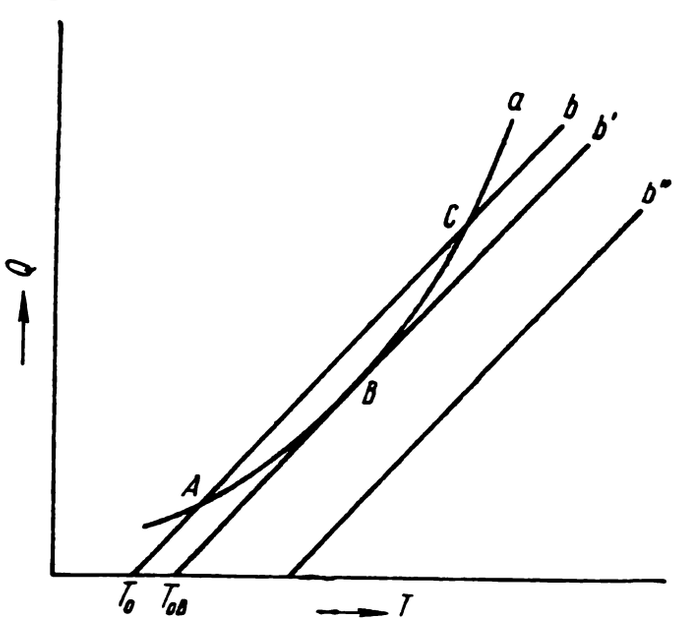


Fig. 1.8. Temperature dependence of quantities of heat liberated and removed in a unit of time

quantity removed in a unit of time. Consequently a system brought to such a state will in a certain time again return to point $A$ owing to self-heating. If the system is in states corresponding to points above point $A$, then as can be seen from the figure, the heat liberated in the vessel in a unit of time will be less than the heat dissipated to the surroundings. Consequently, the system will begin to cool and return to the state characterized by point $A$. If the state of the system is determined by point $C$, then the system brought out of this state will not be able to return to it. State $C$ is consequently a state of unstable equilibrium. Indeed, if the state of the system is characterized by points below point $C$, the liberated heat will be less than the removed heat, the reacting system will cool and, consequently, move away from point $C$. If the state of the system is characterized by points above point $C$, the heat liberated in the vessel will be greater than that removed, and the system will heat, i.e. move away from point $C$ in the opposite direction. If we gradually increase the initial temperature $T_0$ to $T_{0,B}$, only one stationary state corresponding to point $B$ will be possible for the system. At an initial temperature higher than $T_{0,B}$ a stationary process will be impossible. The quantity of heat liberated in a unit of time will be greater than that removed to the surroundings, and the process will proceed only as a non-stationary one with a growing temperature and, consequently, at a growing rate. The condition corresponding to point $B$ is called the *critical condition of ignition*. It is obvious that the conditions of ignition and, in particular, the temperature of ignition, depend on the nature of the combustible mixture, its concentration, the material of the walls and the shape of the vessel, as well as on the nature of the surroundings, since all these factors affect the thermal conditions of the process.

The quantity of heat $Q$ liberated in a vessel in a unit of time is

$$Q = J\overline{Q}V \tag{1.138}$$

where $J$ = rate of chemical reaction
$\overline{Q}$ = heat effect of chemical reaction
$V$ = volume of the vessel.

The rate of a chemical reaction can be written as a function of the temperature and concentrations of the reactants:

$$J = ke^{-E/RT}w(c) \tag{1.139}$$

where $w(c)$ is a certain function of the concentration of the reactants.

Let us see how a process proceeds at comparatively low temperatures, when burning out of the mixture is negligible. In this case the product

$$kw(c)\,V\overline{Q} = B \tag{1.140}$$

can be considered as a constant quantity. Consequently, Eq. (1.138) can be written as

$$Q_1 = Be^{-E/RT} \tag{1.141}$$

The quantity of heat dissipated by the vessel to the surroundings

$$Q_2 = \alpha A\,(T - T_0) \tag{1.142}$$

where $\alpha$ = summary coefficient of heat transfer
$A$ = surface area of vessel.

When a stationary state is reached, we have

$$Q_1 = Q_2 \tag{1.143}$$

or on the basis of Eqs. (1.141) and (1.142)

$$Be^{-E/RT} = L\,(T - T_0) \tag{1.144}$$

where $L = \alpha A$ is the product of constant quantities.

At point $B$ (see Fig. 1.8) the conditions must be observed that

$$Q_1 = Q_2$$

and

$$\frac{dQ_1}{dT}=\frac{dQ_2}{dT} \tag{1.145}$$

or, which is the same

$$Be^{-E/RT_B}=L(T_B-T_0) \tag{1.146}$$

and

$$\frac{BE}{RT_B^2}e^{-E/RT_B}=L \tag{1.147}$$

Inserting Eq. (1.146) into Eq. (1.147), we get

$$\frac{E}{RT_B^2}(T_B-T_0)=1 \tag{1.148}$$

or

$$T_B^2-\frac{E}{R}T_B+\frac{E}{R}T_0=0 \tag{1.149}$$

We find the value of the ignition temperature from the latter equation

$$T_B=\frac{E}{2R}\left(1-\sqrt{1-\frac{4R}{E}T_0}\right) \tag{1.150}$$

The greater root (with a plus sign before the radical) has been discarded, since it corresponds to the region of high temperatures which are usually not achievable in ordinary processes, and for this reason there is no sense in considering it.

It can be seen from Eq. (1.150) that ignition may occur within a limited range of temperatures of the surroundings

$$0\leqslant T_0\leqslant\frac{E}{4R} \tag{1.151}$$

Equality of the radical in Eq. (1.150) to zero corresponds to the maximum value of the ignition temperature, i.e. $T_0 = E/4R$, and

$$T_{B_{max}}=\frac{E}{2R}\approx\frac{E}{4} \tag{1.152}$$

At a temperature of the environment higher than $T_0 = E/4R$, regardless of the conditions of heat transfer, the reaction proceeds in the region of a thermal explosion, i.e. a stationary course of the reaction at such temperatures of the surroundings is impossible.

It follows from Eqs. (1.146) and (1.147) that at the given values of $B$, $L$ and $E$ only one value of the critical ignition temperature $T_B$ is possible at a definite value of $T_0$. Using these equations, we can express the critical ignition temperature through $B$, $L$ and $E$. By graphical solution of Eq. (1.147), we can find the value of $T_B$, after which the value of $T_0$ is uniquely determined from Eq. (1.146).

## *Kinetics of Reactions in a Flow System*

**1.14. General Equation of Rate of Reaction in a Flow System in Ideal Displacement Conditions.** The conducting of reactions in a stream of gas flowing through a tubular reactor is widely used in industry. The reactor may be either hollow, playing the part only of the space where a constant temperature is maintained, or filled

with a layer of a granulated catalyst. Examples of reactions conducted in a flow system on an industrial scale are the reactions of thermal and catalytic cracking of petroleum products, catalytic alkylation, polymerization, the hydro- and dehydrogenization of alcohols, the hydration of olefins, halogenation, nitration with nitrogen oxides, the synthesis of ammonia, the production of sulphuric acid by the contact method, the synthesis of motor fuel, etc. For this reason laboratory experiments for investigating the kinetics of many important industrial reactions are also conducted in flow systems. Since such reactions are usually carried out at a constant pressure and in the

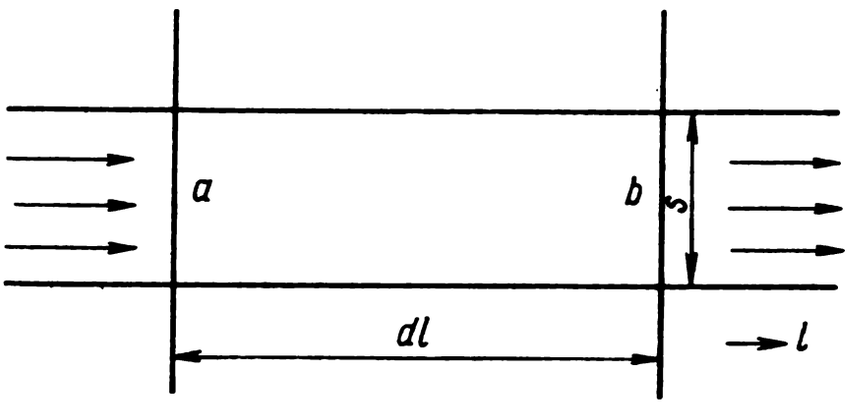


Fig. 1.9. To the calculation of the basic equations for reactions in a flow system

majority of cases are accompanied by a change in the volume of the reactants, the equations for the kinetics of these processes should differ from those derived above for the condition of a constant volume. In addition, the method of calculating the rate constants of reactions proceeding in a flow system should differ from the methods used to calculate the rate constants of reactions proceeding at a constant volume, since it is very difficult to determine the time spent by the reactants in the reaction zone (the so-called contact time).

As shown by G. Panchenkov, the general equations for the kinetics of chemical processes in a flow system can be obtained using the methods of hydrodynamics.

This is very important, since these methods can be used to calculate both stationary and non-stationary processes. The general equations obtained can be used to compute the rates of homogeneous reactions of any orders and any type (irreversible, reversible, concurrent, consecutive, autocatalytic, chain, etc.) and heterogeneous reactions (see below).

Let us consider the basic equations for processes in a flow system on condition that there is no mixing, i.e. conditions of ideal displacement are observed, and also the applicability of the equations obtained in specific cases.

Let us consider the flow of a substance through sections *a* and *b* at a distance of *dl* from each other (Fig. 1.9). To simplify calculations,

we shall assume that the temperature of the substance is constant, and neglect transportation due to diffusion and the action of dissipative forces, i.e. viscosity and thermal conductivity. Let the cross-sectional area of the flow in the reactor be 1 $cm^2$, the linear velocity of the substance be $u$ and the concentration of substance $A_i$ in the same section $c_{A_i}$. During the time $dt$ an amount of substance $A_i$ equal to $c_{A_i}\,udt$ will flow through a unit of area of the first section ($a$), and an amount of this substance equal to $\left[c_{A_i}u - \frac{\partial (c_{A_i}u)}{\partial l}\,dl\right] dt$ through a unit of area of the second section ($b$), since part of the substance remains in the elementary volume being considered (at the initial moment the reactor was empty). The difference between the amounts of the substance emerging from the element of volume $dl$ and that entering it (if no reaction occurs in it) will be equal to $-\frac{\partial (c_{A_i}u)}{\partial l}\,dl\,dt$. If a reaction of the type

$$\nu_1 A_1 + \nu_2 A_2 + \ldots = \nu_1' A_1' + \nu_2' A_2' + \ldots \tag{1.153}$$

occurs between the molecules of the substance in the reaction tube, this will also cause the amount of substance $A_i$ entering the element of volume being considered to differ from the emerging amount. Thus, in the general case (when a chemical reaction takes place in the flowing substance), the difference between the amount of emerging substance and that entering, equal to the change in the total amount of substance in the given volume, will be

$$-\frac{\partial (c_{A_i}u)}{\partial l}\,dl\,dt - J\,dl\,dt = \frac{\partial c_{A_i}}{\partial t}\,dl\,dt \tag{1.154}$$

where $J$ is the rate of the chemical reaction determined with respect to substance $A_i$ (the amount of this substance reacting in a unit of time in a unit of volume).

Equation (1.154) can be rewritten in the form

$$-\frac{\partial}{\partial l}(c_{A_i}u) - J = \frac{\partial c_{A_i}}{\partial t} \tag{1.155}$$

We write the partial derivatives in these equations because we are considering the process in a given element of volume. Equation (1.155) is the so-called *equation of continuity* expressing the law of conservation of matter. Using vector notation, this equation can be written as

$$-\operatorname{div}(c_{A_i}u) - J = \frac{\partial c_{A_i}}{\partial t} \tag{1.156}$$

and it can be used for calculating non-stationary processes.

If the amounts of the reactants fed into the reaction tube are constant, a stationary process will set in in a certain time after the beginning of feeding these reactants into the tube. In a stationary process the concentrations in the given element of volume do not change with time, i.e.

$$\frac{\partial c_{A_i}}{\partial t} = 0 \tag{1.157}$$

After the process becomes stationary, the concentrations $c_{A_i}$ of any of the reactants and the linear velocity $u$ of a substance in a given section of the tube will be uniquely determined only by the distance $l$ to this section from the beginning of the reaction zone, i.e.

$$\left.\begin{aligned} c_{A_i} &= \varphi(l) \\ u &= \psi(l) \end{aligned}\right\} \tag{1.158}$$

For this reason Eqs. (1.155) and (1.156) for the stationary state will be written as follows:

$$\left.\begin{aligned} -\frac{d(c_{A_i}u)}{dl} &= J \\ -\operatorname{div}(c_{A_i}u) &= J \end{aligned}\right\} \tag{1.159}$$

Let us find the concentration of the $i$-th component at a known distance from the beginning of the tube:

$$c_{A_i} = \frac{n_{A_i}}{V} \tag{1.160}$$

where $n_{A_i}$ = number of moles of substance $A_i$ flowing through the given section in a unit of time

$V$ = volume of the substance flowing in a unit of time through the same section.

The linear velocity $u$ can be expressed as

$$u = \frac{V}{A_t} \tag{1.161}$$

where $A_t$ is the cross-sectional area of the tube.

Inserting Eqs. (1.160) and (1.161) into the first equation (1.159) and considering $A_t$ to be constant, we get

$$-\frac{1}{A_t}\frac{dn_{A_i}}{dl} = J \tag{1.162}$$

But $n_{A_i} = n_{0,\,A_i}(1 - x)$, where $n_{0,\,A_i}$ is the number of moles of substance $A_i$ entering the reaction zone in a unit of time, and $x$ is the amount of reacted substance $A_i$ at the distance $l$ from the beginning of the reaction zone, expressed as a fraction of the initial

amount. Consequently

$$-\frac{dn_{A_i}}{dl}=n_{0,\,A_i}\frac{dx}{dl} \tag{1.163}$$

Inserting Eq. (1.163) into Eq. (1.162), we have

$$n_{0,\,A_i}\frac{dx}{A_t\,dl}=J \tag{1.164}$$

This is the equation of the kinetics of any chemical reaction proceeding in a flow system, written in a general form. Using the basic postulate of chemical kinetics, Eq. (1.164) for irreversible reactions can be written as

$$n_{0,\,A_i}\frac{dx}{A_t\,dl}=kc_{A_1}^{\nu_1}c_{A_2}^{\nu_2}\ldots c_{A_n}^{\nu_n} \tag{1.165}$$

For reversible reactions it has the form

$$n_{0,\,A_i}\frac{dx}{A_t dl}=k_1c_{A_1}^{\nu_1}c_{A_2}^{\nu_2}\ldots c_{A_n}^{\nu_n}-k_2c_{A_1'}^{\nu_1'}c_{A_2'}^{\nu_2'}\ldots c_{A_n'}^{\nu_n'} \tag{1.166}$$

where $k_1$ and $k_2$ are rate constants of the forward and reverse reactions.

To integrate Eqs. (1.165) and (1.166), the concentrations must be expressed as a function of $l$. This is easy to do if the reaction proceeds in a flow of gases, especially ideal ones. Thus

$$V=\frac{\sum n_iRT}{P} \tag{1.167}$$

and, consequently,

$$c_{A_i}=\frac{n_{0,\,A_i}(1-x)P}{\sum n_iRT} \tag{1.168}$$

Here $\sum n_i$ = total number of moles of all the substances participating in the reaction (both reactants and products) passing through a given section in a unit of time[1]

[1] For the reaction described by Eq. (1.153), on condition that the concentrations of the products at the initial moment are equal to zero, we have

$$\sum n_i=n_{0,\,A_i}(\alpha+\beta x)$$

where

$$\alpha=\frac{n_{0,\,A_1}}{n_{0,\,A_i}}+\frac{n_{0,\,A_2}}{n_{0,\,A_i}}+\ldots+\frac{n_{0,\,A_n}}{n_{0,\,A_i}}$$

and

$$\beta=\frac{\nu_1'}{\nu_i}+\frac{\nu_2'}{\nu_i}+\ldots+\frac{\nu_n'}{\nu_i}-\frac{\nu_1}{\nu_i}-\frac{\nu_2}{\nu_i}-\ldots-\frac{\nu_n}{\nu_i}$$

here $n_{0,\,A_i}$ is the number of moles of substance $A_i$ entering the reaction zone in a unit of time.

$P$ = total pressure of the mixture of all the gases, which in the general case is a function of the distance $l$ from the beginning of the reaction zone, i.e.

$$P = f(l) \tag{1.169}$$

This function must be known to integrate Eqs. (1.167) and (1.166). It is easy to determine its form, since the pressure at the beginning and the end of the reaction zone is usually preset in laboratory and industrial reaction apparatus. Most frequently the pressure difference $\Delta P$ between the beginning and the end of the reaction zone is not great, and, therefore, the value of $\Delta P$ may be neglected and the pressure $P$ considered as constant.

If the reacting gas is greatly diluted with an inert gas, i.e. the change in the volume due to the chemical reaction may be neglected, or the chemical reaction proceeds without a change in the volume, or the reaction proceeds in a liquid flow system, then the volume rate of flow will be a constant quantity; hence at a constant value of $A_t$ we have

$$\frac{du}{dl} = 0 \tag{1.170}$$

Therefore Eq. (1.159) becomes

$$-u\frac{dc_{A_i}}{dl} = J \tag{1.171}$$

Inserting into Eq. (1.171) the value of the derivative $dc_{A_i}/dl$ and taking into account condition (1.161), we get

$$-\frac{dn_{A_i}}{A_t\,dl} = J \tag{1.172}$$

Equation (1.172) is identical to Eq. (1.162). The difference between these equations is that in Eq. (1.162) the volume of the gas $V$ flowing through the given section in a unit of time is a function of the distance $l$ from the beginning of the reaction zone, and in Eq. (1.172) it is a constant quantity.

In Eqs. (1.162), (1.165), (1.166) and (1.172) the quantity $A_t\,dl$ can be replaced by an element of volume $dV$ of the space in which the reaction proceeds, i.e. we can write that

$$A_t\,dl = dV \tag{1.173}$$

This substitution makes it possible to use the equations indicated above for calculating the volume of a reactor required for achieving the given degree of transformation $x$. Obviously, for this purpose it is essential to previously determine the rate constants of the given reaction.

For non-isothermal processes, which are frequently used in industrial reactors, the rate constant must be expressed with the aid of the Arrhenius equation as a function of the temperature and on the basis of experimental data the dependence of the temperature on the distance along the tube within the limits of the reaction zone must be set.

Below are considered several examples of irreversible reactions in a homogeneous gaseous medium in conditions of ideal displacement.

**1.15. Irreversible Reaction of the First Order.** Such a reaction can be written in the general form as

$$A \rightarrow \nu_1 A_1 + \nu_2 A_2 + \ldots + \nu_n A_n$$

Hence Eq. (1.165) with account of Eq. (1.168) and the footnote on page 59 acquires the form

$$n_{0,A} \frac{dx}{A_t\, dl} = k \frac{(1-x)P}{(1+\beta x)RT} \tag{1.174}$$

Separating variables and integrating this expression within the limits from 0 to $x$ and from 0 to $l$, we get

$$-(1+\beta)\ln(1-x) - \beta x = \frac{kA_t P}{n_{0,A}RT}\, l \tag{1.175}$$

whence

$$k = n_{0,A}\frac{RT}{PV}\left[-(1+\beta)\ln(1-x) - \beta x\right] \tag{1.176}$$

where $V = A_t l$ is the volume of the reaction space.

For a reaction of the type $A_1 \rightarrow A_2$ Eq. (1.176) becomes

$$k = n_{0,A}\frac{RT}{PV}\ln\frac{1}{1-x} \tag{1.177}$$

since $\beta = 0$.

Comparing Eqs. (1.177) and (1.12), we see that $n_{0,A}\frac{RT}{PV} = \frac{1}{t}$, i.e. the time spent by the substance in the reaction zone or, in the given case, the duration of contact

$$t = \frac{PV}{n_{0,A}RT} \tag{1.178}$$

It is the most convenient to check how close the results of calculations according to Eq. (1.176) coincide with experimental data and determine the values of the constants as follows. Equation (1.176) can be written as

$$n_{0,A}x = -n_{0,A}\frac{1+\beta}{\beta}\ln(1-x) - k\frac{PV}{\beta RT} \tag{1.179}$$

Let us introduce the notation $n_{0,A}\,x = z$ and $-n_{0,A}\ln(1-x) = y$. Equation (1.179) will now describe a straight line (Fig. 1.10). The section cut off by the straight line on the axis of ordinates is equal to $-k\frac{PV}{\beta RT}$, and the tangent of the angle $\varphi$ of inclination of the line $\tan\varphi = \frac{1+\beta}{\beta}$.

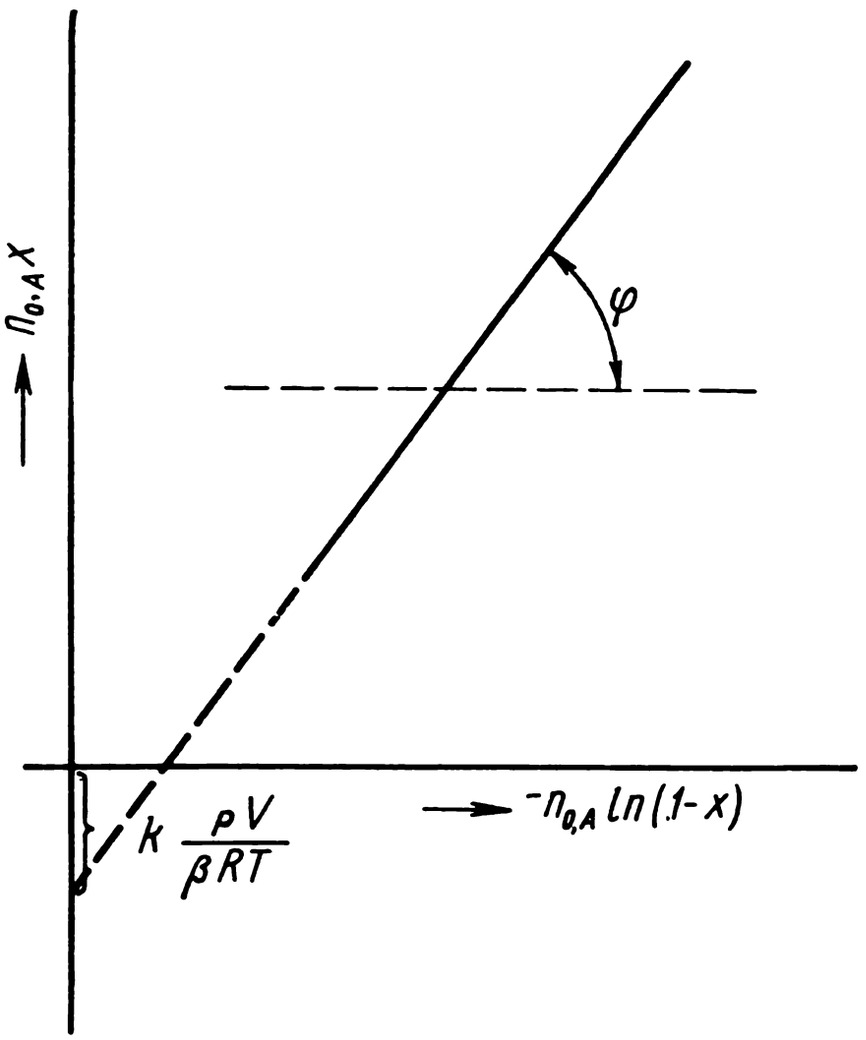


Fig. 1.10. Dependence of $n_{0,A}x$ on $-n_{0,A}\ln(1-x)$ for reactions of the first order proceeding in a flow system

The value of $\beta$ is easily found from the latter expression. Knowing $\beta$, we can readily compute the value of $k$ from the section cut off on the axis of ordinates.

The kinetics of the reaction of thermal cracking of *n*-hexadecane (Fig. 1.11) obeys this equation if it is judged according to the amount of untransformed *n*-hexadecane at different rates of feeding it into the reaction zone (according to data obtained by G. Panchenkov and V. Baranov).

**1.16. Irreversible Reaction of the Second Order.** Assume that a reaction of the type $A + B \rightarrow C + D$ proceeds in a flow system.

If the number of moles of substances A and B fed into the reaction zone in a unit of time is respectively equal to $n_{0,A}$ and $n_{0,B}$, Eq. (1.165) with account of Eq. (1.168) becomes

$$\frac{dx}{dl} = k\frac{A_t P^2}{R^2T^2}\frac{(1-x)(n_{0,B}-n_{0,A}x)}{(n_{0,A}+n_{0,B})} \tag{1.180}$$

Separation of variables and integration gives

$$k = \frac{(n_{0,A}+n_{0,B})^2}{(n_{0,A}-n_{0,B})}\frac{R^2T^2}{VP^2}\ln\frac{n_{0,B}(1-x)}{(n_{0,B}-n_{0,A}x)} \tag{1.181}$$

If the initial concentrations of both substances are the same, integration of Eq. (1.180) gives

$$k = 4n_{0,A}\frac{R^2T^2}{VP^2}\frac{x}{1-x} \tag{1.182}$$

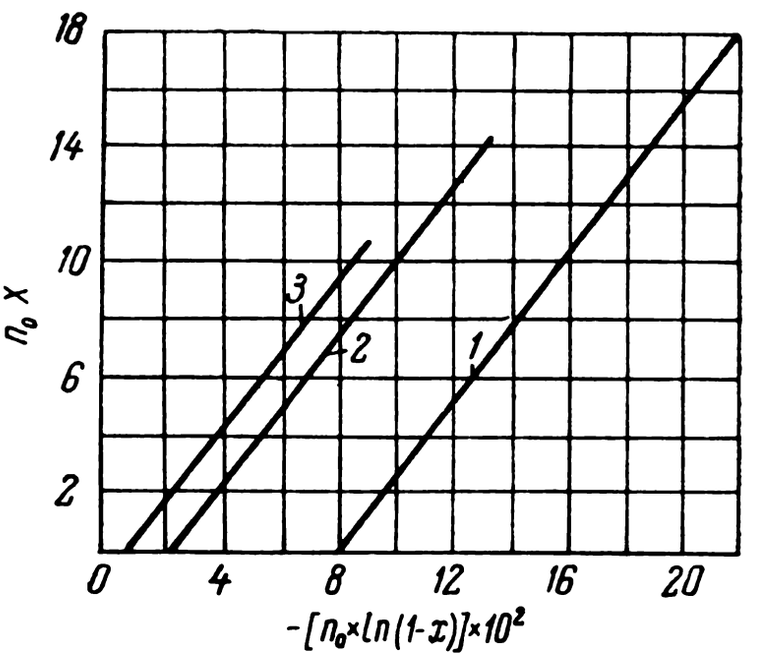


Fig. 1.11. Kinetics of thermal cracking of *n*-hexadecane in a flow system:
*1*—at 520 °C; *2*—at 550 °C; *3*—at 580 °C

**1.17. Reversible Reaction of the First Order.** A reversible reaction, as noted previously, can formally be considered as an irreversible one if we assume that not all of the initial substance $n_{0,A}$ reacts, but the difference between the initial amount of the substance and the amount that remained unreacted by the moment when equilibrium set in. Here Eq. (1.166) with account of Eq. (1.168) becomes

$$\frac{dx}{A_t\,dl} = k\frac{1-n_{\infty,A_1}-x}{n_{0,A_1}RT}P \tag{1.183}$$

where $n_{\infty,A_1} = \frac{n'_{\infty,A_1}}{n_{0,A_1}}$; $n'_{\infty,A_1}$ is the number of moles of substance $A_1$ formed by the moment when equilibrium sets in.

Integration of this equation yields

$$k = n_{0,A_1}\frac{RT}{PV}\ln\frac{1-n_{\infty,A_1}}{1-n_{\infty,A_1}-x} \tag{1.184}$$

Here $k = k_1 + k_2$ (where $k_1$ and $k_2$ are the rate constants of the forward and reverse reactions).

**1.18. Reversible Reaction of the Second Order.** If a reaction of the type $A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + D$ proceeds in a flow system, Eq. (1.166) with account of Eq. (1.168), on condition that only substances A and B are present at the initial moment, becomes

$$\frac{dx}{A_t\,dl} = k_1 \frac{P^2}{R^2T^2} \frac{(1-x)(n_{0,\,B} - n_{0,\,A}x)}{(n_{0,\,A} + n_{0,\,B})^2} - k_2 \frac{P^2}{R^2T^2} \frac{n_{0,\,A}x^2}{(n_{0,\,A} + n_{0,\,B})^2} \qquad (1.185)$$

where $n_{0,\,A}$ and $n_{0,\,B}$ are the number of moles of substances A and B, respectively, entering the reaction zone in a unit of time.

Integration yields

$$k_1 - k_2 = (n_{0,\,A} + n_{0,\,B})^2 \frac{R^2T^2}{P^2V(m_1 - m_2)} \ln \frac{m_2(m_1 - x)}{m_1(m_2 - x)} \qquad (1.186)$$

where $m_{1,\,2} = \dfrac{n_{0,\,A} - n_{0,B} \pm \sqrt{(n_{0,A} - n_{0,B})^2 - 4n_{0,A}n_{0,B}(1-K')}}{2n_{0,A}(1-K')}$

$K' = \dfrac{k_2}{k_1}$ is the equilibrium constant[1].

**1.19. Consecutive Reaction.** The rate constants for a homogeneous consecutive irreversible reaction conducted in a flow system can easily be calculated. Let us consider a consecutive irreversible reaction of the type $A \xrightarrow{k_1} \nu_1 B \xrightarrow{k_2} \nu_2 C$ (where $k_1$ and $k_2$ are the rate constants of the corresponding reactions). Assume that at the initial moment we have only substance A. At a certain distance $l$ from the beginning of the reaction zone, the number of moles of substance A will be $n_{0,\,A}(1-x)$, where $n_{0,\,A}$ is the number of moles of this substance entering the reaction zone in a unit of time. As follows from the chemical equation, $\nu_1 n_0 x$ moles of substance B should be formed, of which $n_0 y$ moles transform into substance C. Thus the number of moles of substance B passing through the same section in a unit of time will be $n_0(\nu_1 x - y)$. According to the chemical equation, $\frac{\nu_2}{\nu_1} n_0 y$ moles of substance C form. Summation of these values gives

$$\sum n = n_{0,\,A}\left[1 + (\nu_1 - 1)x + \left(\frac{\nu_2}{\nu_1} - 1\right)y\right] \qquad (1.187)$$

[1] Not the ratio $k_2/k_1$, but its reciprocal $k_1/k_2$ should have been substituted as the equilibrium constant; as a result the equilibrium constant would be written as is general practice at present, i.e. with the concentrations of the products in the numerator of the fraction. In this case, however, Eq. (1.186) would be too complicated. This is why we have inserted here a quantity that is the reciprocal of the usual equilibrium constant, i.e. $K' = k_2/k_1 = 1/K$.

Using Eq. (1.168), we find

$$c_A = \frac{(1-x)P}{\left[1+(\nu_1-1)x+\left(\frac{\nu_2}{\nu_1}-1\right)y\right]RT} \tag{1.188}$$

and

$$c_B = \frac{(\nu_1 x - y)P}{\left[1+(\nu_1-1)x+\left(\frac{\nu_2}{\nu_1}-1\right)y\right]RT} \tag{1.189}$$

Using Eq. (1.165) for two consecutive reactions and assuming that the second reaction is also of the first order, upon determining its rate according to the amount of substance C formed, we get

$$n_{0,A}\frac{dx}{A_t\,dl} = k_1 \frac{(1-x)P}{\left[1+(\nu_1-1)x+\left(\frac{\nu_2}{\nu_1}-1\right)y\right]RT} \tag{1.190}$$

$$n_{0,A}\frac{dy}{A_t\,dl} = k_2\frac{\nu_1}{\nu_2}\frac{(\nu_1 x - y)P}{\left[1+(\nu_1-1)x+\left(\frac{\nu_2}{\nu_1}-1\right)y\right]RT} \tag{1.191}$$

Dividing Eq. (1.191) by Eq. (1.190), we get

$$\frac{dy}{dx} = K\frac{\nu_1 x - y}{1-x} \tag{1.192}$$

where $K = k_2\nu_1/k_1\nu_2$.

Solution of the non-homogeneous linear differential equation

$$y' + f(x)\,y = g(x) \tag{1.193}$$

gives

$$\nu_1 x - y = \frac{\nu_1}{1-K}\left[(1-x)^K - (1-x)\right] \tag{1.194}$$

The solution of Eq. (1.193) has the form

$$y = e^{-F(x)}\left(B + \int_0^x g(x)\,e^{F(x)}\,dx\right) \tag{1.195}$$

where

$$F(x) = \int_0^x f(x)\,dx$$

For Eq. (1.192)

$$f(x) = \frac{K}{1-x}$$

and

$$g(x) = \frac{K\nu_1 x}{1-x} \tag{1.196}$$

Consequently

$$F(x) = \int_0^x \frac{K\,dx}{1-x} = -K\ln(1-x)$$

and

$$e^{-F(x)} = e^{K \ln(1-x)}$$

Transformation of the last equation gives

$$e^{F(x)} = (1-x)^{-K} \tag{1.197}$$

The value of the integral in Eq. (1.195) will be

$$\int_0^x g(x)\, e^{F(x)}\, dx = K \int_0^x \frac{\nu_1 x}{1-x} (1-x)^{-K}\, dx = K\nu_1 \int_0^x x(1-x)^{-(K+1)}\, dx$$

The last integral is easily taken by parts. Integration yields

$$K\nu_1 \int_0^x x(1-x)^{-(K+1)}\, dx = \frac{\nu_1 x}{(1-x)^K} + \frac{\nu_1}{1-K}(1-x)^{1-K} - \frac{\nu_1}{1-K} \tag{1.198}$$

Inserting Eqs. (1.197) and (1.198) into Eq. (1.195), we get

$$y = (1-x)^K \left[ B + \frac{\nu_1 x}{(1-x)^K} + \frac{\nu_1 (1-x)^{1-K}}{1-K} - \frac{\nu_1}{1-K} \right] \tag{1.199}$$

From the initial conditions ($y = 0$ at $x = 0$) we have

$$B = 0 \tag{1.200}$$

It directly follows from Eq. (1.199) that

$$\nu_1 x - y = \frac{\nu_1}{1-K} [(1-x)^K - (1-x)]$$

At the point of the maximum

$$\frac{d(\nu_1 x - y)}{dx} = 0$$

Taking the derivative of Eq. (1.194) and equating it to zero, we get

$$(1-x_m)^{K-1} = \frac{1}{K} \tag{1.201}$$

where $x_m$ is the amount of reacted substance A corresponding to the maximum yield of substance B.

Inserting $y$ from Eq. (1.194) into Eq. (1.190), separating variables and integrating, we get

$$k_1 = n_{0,A} \frac{RT}{PV(1-K)} \left\{ -\nu_2 (1-K) \ln(1-x) - \right.$$

$$\left. - [\nu_1 - 1 + K(1-\nu_2)]\, x + \frac{\nu_2 - \nu_1}{K}(1-x)^K - \frac{\nu_2 - \nu_1}{K} \right\} \tag{1.202}$$

This equation makes it possible to calculate the rate constant for the first reaction. The value of the rate constant $k_2$ for the second reaction is found from the expression $K = k_2\nu_1/k_1\nu_2$.

# CHAPTER 2

# GENERAL LAWS OF THE DECOMPOSITION AND FORMATION OF MOLECULES

**2.1. Elementary Chemical Processes.** A chemical reaction consists of a number of intermediate processes in which molecules of the reactants and separate atoms, radicals, ions, excited atoms or molecules appearing upon initiation of the reaction and during its course participate. Intermediate processes proceeding in one stage are called *elementary chemical processes.* The detailed mechanism of chemical reactions, i.e. all the steps or stages which they consist of, is not known in the majority of cases, since it is very difficult to experimentally discover intermediates which are usually unstable (have a high reactivity).

Only in rare cases do the reactant molecules react directly. An example of such a direct reaction is that of decomposition of hydrogen iodide. Upon the collision of two molecules of hydrogen iodide having sufficient energy and appropriately mutually oriented, the bonds H—I break and new bonds appear between the atoms of hydrogen and iodine with the formation of molecular hydrogen and iodine. An example of reactions for which all the elementary processes, i.e. all the intermediate chemical reactions, are known are reactions between vapours of alkali metals and halogens (the so-called reactions in a rarefied flame, see Sec. 4.8).

In studying the kinetics of many reactions, we shall as far as possible consider elementary chemical processes. In this chapter we shall study only certain elementary processes of the decomposition and formation of molecules that are of importance for many chemical reactions.

**2.2. Dissociation of Molecules under the Action of Light (Photochemical Dissociation).** The simplest elementary chemical process is the dissociation of molecules under the action of light. This process leads to the appearance of continuous absorption zones in the molecular spectra. This is explained by the fact that a molecule decomposes into its constituent parts, therefore the absorption of light no longer obeys the laws of quantum mechanics (the kinetic energy of the particles—the dissociation products—is not quantized). The boundary of the continuum (continuous part) in the line and band absorption spectrum corresponds to the minimum energy of light quanta $h\nu_q$ that is sufficient to cause dissociation.

Having determined the frequency corresponding to the place of merging of the bands, we can calculate the energy of dissociation. For molecules with a covalent bond, a greater energy than that of dissociation corresponds to the place of merging of the borders and the appearance of a continuous absorption zone. Such disagreement between spectroscopic and thermochemical data is explained by the fact that, for example, a diatomic molecule decomposes under the action of light into one normal and one excited atom. This statement can be verified by considering the potential curves of the normal and excited state. A glance at Fig. 2.1 shows that the energy $D_{chem}$ required for decomposition of a molecule into two unexcited atoms is less than that spent for photochemical dissociation, equal to $A(y) + D(y)$. This is explained by the fact that in photochemical dissociation electronic excitation of a molecule occurs, and the excited molecule may be in states with an energy greater than that of dissociation in the excited state, owing to which it decomposes into atoms. It thus follows from the potential energy curves that

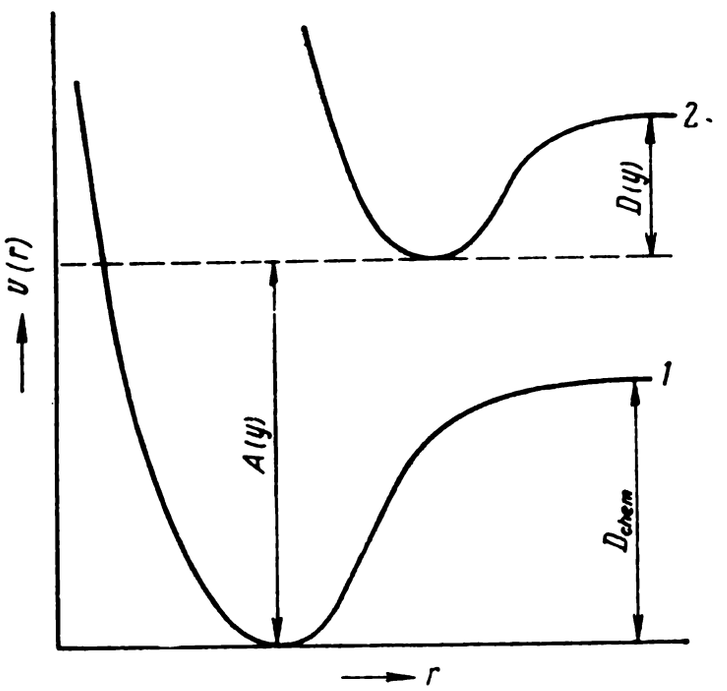


Fig. 2.1. Potential curves for diatomic molecule with a covalent bond:
1—normal state; 2—excited state

$$D_{chem} < A(y) + D(y) \quad (2.1)$$

For an $I_2$ molecule a quantum with an energy of 2.4 eV ($\nu = 2050\ cm^{-1}$) corresponds to the place of merging of the bands. The energy of dissociation of an iodine molecule according to thermochemical data is 1.5 eV (36.09 kcal/mol).

It is obvious that the energy of electronic excitation of one of the iodine atoms appearing as a result of dissociation of a molecule should be equal to 2.4 eV — 1.5 eV = 0.9 eV. The energy of the metastable state, greater than that of the normal state $^2P_1$ by 0.94 eV, corresponds to such an energy level of the atom. If this circumstance is taken into consideration, it is easy to see that the value of the energy of dissociation determined on the basis of spectroscopic data well agrees with the value of the energy found by the thermochemical method.

The results obtained can also be demonstrated with the aid of the diagram shown in Fig. 2.2. Let us lay off vertically the vibration

levels of the normal and excited states. The place where these levels merge will correspond to the maximum vibration energy which a molecule in the given state can have. All the following states are not quantized, since the molecule decomposes into atoms. These unquantized levels are shaded with diagonal lines. If a molecule in the basic electronic state could decompose into atoms, the energy of its dissociation would correspond to $D_{chem}$ coinciding with the value of the energy found on the basis of thermochemical data. But photochemical decomposition occurs as a result of electronic excitation caused by the absorption of a light quantum. The energy necessary for decomposition of a molecule under the action of absorbed light should correspond to the quantity $h\nu_q$. This will be a quantum corresponding to the place of merging of the bands. The quantities $h\nu_e$ and $h\nu_a$ correspond to the energies of electronic excitation of a molecule and the products of its decomposition. The quantity $D(y)$ corresponds to the energy of dissociation of a molecule in the excited state. Thus, knowing the electron levels appearing upon the dissociation of atoms, we can determine the energy of dissociation according to the position of the boundary of the continuous absorption zone.

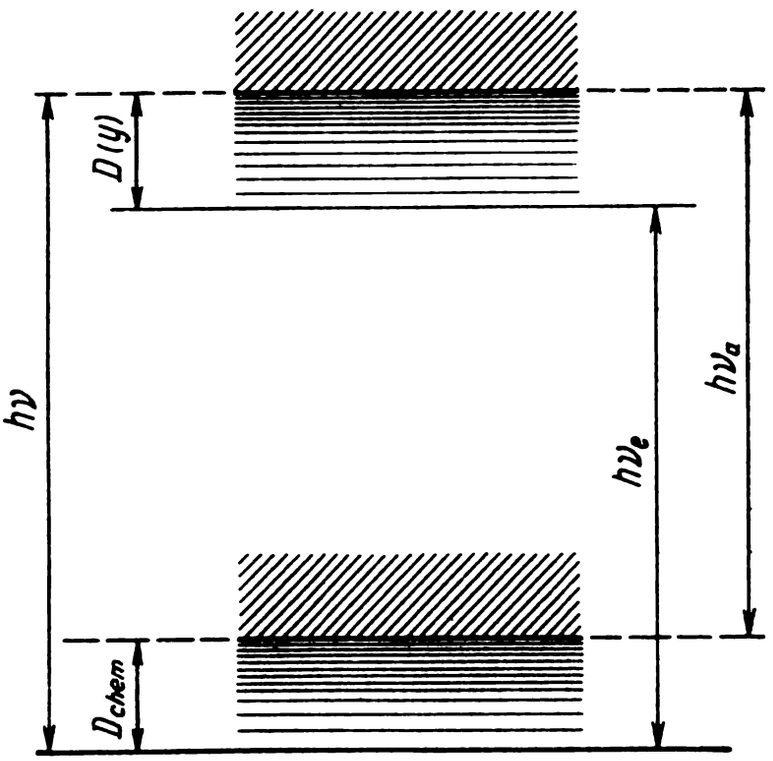


Fig. 2.2. Diagram showing arrangement of vibration levels for normal and excited states of a diatomic molecule

For molecules with an ionic bond, the frequency corresponding to the place of merging of the borders in absorption spectra directly gives the dissociation energy $D_{chem}$. This occurs owing to the fact that the excitation of a molecule with an ionic bond leads to the transition of an electron from the anion to the cation. Consequently, decomposition of an excited molecule leads to the formation of neutral atoms. This conclusion is well illustrated by the potential curves for the normal and excited states of a molecule with an ionic bond (Fig. 2.3). It can be seen from the figure that

$$D_{chem} = D(y) + A(y) \qquad (2.2)$$

Frequently owing to the complicated nature of the spectrum,

and also to the broadening of the bands and a great reduction in their intensity, it is more convenient to determine the dissociation energy by calculating the place of band merging with the aid of a special formula.

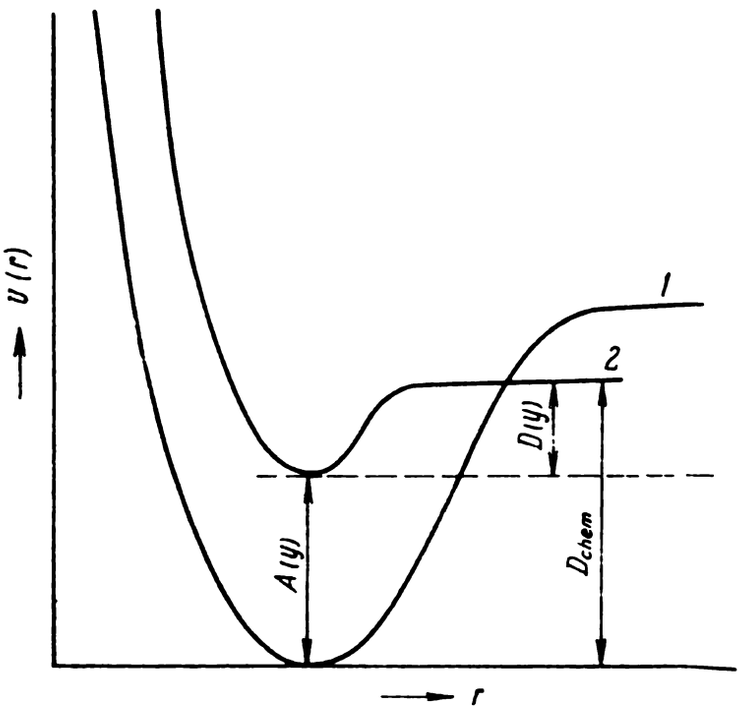


Fig. 2.3. Potential curves for diatomic molecule with an ionic bond:
*1*—normal state; *2*—excited state

Upon electron transitions the fundamental natural frequencies of vibrations of a molecule change. Let us denote the frequency in the basic electronic state by $\omega''$ and in the excited one by $\omega'$. According to the theory of molecular vibrations, the sum of the electronic and vibrational energy in these states can be determined by the following formulas:

$$E' = E'_e + \left(n'_v + \frac{1}{2}\right) h\omega' - \alpha' h\omega' \left(n'_v + \frac{1}{2}\right)^2 \quad (2.3)$$

$$E'' = E''_e + \left(n''_v + \frac{1}{2}\right) h\omega'' - \alpha'' h\omega'' \left(n''_v + \frac{1}{2}\right)^2 \quad (2.4)$$

where $n'_v$ and $n''_v$ = quantum numbers of vibrational levels of an unexcited and an excited molecule, respectively
$\alpha'$ and $\alpha''$ = corresponding anharmonic (cross) ratios.

From Eqs. (2.3) and (2.4) we can determine the frequencies of the corresponding spectral lines:

$$\nu = \nu_e + \left[\left(n'_v + \frac{1}{2}\right)\omega' - \left(n''_v + \frac{1}{2}\right)\omega''\right] - \left[\left(n'_v + \frac{1}{2}\right)^2 \alpha'\omega' - \left(n''_v + \frac{1}{2}\right)^2 \alpha''\omega''\right] \quad (2.5)$$

This expression is easily transformed into the following one:

$$\nu = \nu_0 + (a'n'_v - b'n'^2_v) - (a''n''_v - b''n''^2_v) \quad (2.6)$$

where $\nu_0 = \nu_e + \frac{1}{2}\omega' - \frac{1}{2}\omega'' - \frac{1}{4}\omega'\alpha' + \frac{1}{4}\omega''\alpha''$

$$a' = \omega' - \alpha'\omega'; \quad a'' = \omega'' - \alpha''\omega''$$
$$b' = \alpha'\omega'; \quad b'' = \alpha''\omega''$$

If there are electron transitions, the transitions $\Delta n_v = n'_v - n''_v$ may be any ones. But each change gives a band, consequently each electron transition also leads to the formation of a system of bands. It follows from Eq. (2.6) that when $n''_v = 0$ we have

$$\nu = \nu_e + a'n'_v - b'n'^2_v \quad (2.7)$$

Thus the dependence of $\nu$ (the wave number of the zero line of the band) on $n_v$ is not a linear, but a parabolic one, and the distances between the levels redu-

ce with an increase in the values of $n'_v$ (Fig. 2.4). The curve $\alpha\alpha'$ characterizing the transitions from the level $n'_v = 0$ to any other level $n'_v$ passes through a maximum (Fig. 2.4 shows part of the curve before the maximum). The beginning of the continuous absorption zone corresponds to the maximum of curve $\alpha\alpha'$.

At the point of the maximum of curve $\alpha\alpha'$ we have

$$\frac{d\nu}{dn'_v} = 0 \qquad (2.8)$$

Taking the derivative of Eq. (2.7) with respect to $n'_v$, we get

$$\frac{d\nu}{dn'_v} = a' - 2b'n'_v \qquad (2.9)$$

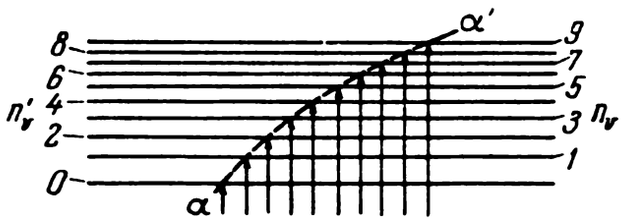


Fig. 2.4. Dependence of distances between vibrational levels on $n'_v$

At the point of the maximum, this derivative should be equal to zero, i.e.

$$a' - 2b'n'_{v_{max}} = 0 \qquad (2.10)$$

whence

$$n_{v_{max}} = \frac{a'}{2b'} \qquad (2.11)$$

Inserting Eq. (2.11) into Eq. (2.7), we get

$$\nu_{max} = \nu_e + \frac{a'^2}{2b'} - \frac{a'^2}{4b'} = \nu_e + \frac{a'^2}{4b'} \qquad (2.12)$$

The value of $\nu_{max}$ determines the boundary of the zone of continuous absorption. Consequently, this quantity can be used to calculate the energy $\varepsilon_k$ required for photochemical dissociation:

$$\varepsilon_k = h\nu_{max}$$

Knowing $\varepsilon_k$ and the value of the energy of excitation of an appearing atom, we can calculate the energy of dissociation of a molecule.

Let us consider this method of determining the energy of dissociation on the example of molecular bromine. The bromine band is described by the equation

$$\nu' = 16\,463 + (151n'_v - 1.82n'^2_v) - (326.6n''_v - 1.72n''^2_v)$$

where $\nu'$ is the wave number.

Let us consider transitions for which $n''_v = 0$. Here

$$\nu' = 16\,463 + 151n'_v - 1.82n'^2_v \qquad (2.13)$$

At the maximum point

$$\frac{d\nu'}{dn'_v} = 151 - 3.64n'_{v_{max}} = 0$$

whence

$$n'_{v_{max}} = 41.48$$

Inserting this value of $n'_{v_{max}}$ into Eq. (2.13), we get

$$\nu'_{max} = 19\,595 \text{ cm}^{-1}; \quad \lambda_{min} = 5.105 \text{ Å};$$
$$\varepsilon = 2.434 \text{ eV} = 56.05 \text{ kcal/mol}$$

The energy of excitation of an appearing bromine atom is 0.454 eV, therefore the energy of dissociation of a bromine molecule $D = 2.434$ eV $- 0.454$ eV $= 1980$ eV $= 45.62$ kcal/mol.

The energy of dissociation of a diatomic molecule can sometimes be calculated as follows. As already indicated previously, the vibrational energy ($E_v$) of a molecule is

$$E_v = \left[\left(n_v + \frac{1}{2}\right) - \alpha\left(n_v + \frac{1}{2}\right)^2\right] h\omega$$

Introducing the symbol $z = n_v + \frac{1}{2}$, we get

$$E_v = h\omega\,(z - \alpha z^2) \tag{2.14}$$

This expression can be used to determine the maximum value of the vibrational energy possible for a given molecule. For this purpose $dE_v/dz$ should be equated to zero, which makes it possible to determine the maximum possible value of the vibration quantum number for the given molecule.

It is easy to see that

$$\frac{dE_v}{dz} = h\omega\,(1 - 2\alpha z_{max}) = 0$$

whence

$$z_{max} = \frac{1}{2\alpha} \tag{2.15}$$

Inserting Eq. (2.15) into Eq. (2.14), we get

$$E_{v_{max}} = h\frac{\omega}{4\alpha} \tag{2.16}$$

It is obvious that

$$E_{v_{max}} = hD \tag{2.17}$$

From Eqs. (2.16) and (2.17), we get

$$D = \frac{\omega}{4\alpha} \tag{2.18}$$

Thus, to determine the energy of dissociation it is necessary to know the fundamental frequency of vibrations $\omega$ and the anharmonic ratio $\alpha$.

The quantities $\omega$ and $\alpha$ are determined from spectroscopic data. For example, for gaseous hydrogen chloride it was found that the bands correspond to the following frequencies: $0.867 \times 10^{14}$, $1.705 \times 10^{14}$ and $2.521 \times 10^{14}$ s$^{-1}$. It is general knowledge that

$$E'_v - E''_v = (n'_v - n''_v)\,h\omega - \alpha h\omega\left[\left(n'_v + \frac{1}{2}\right)^2 - \left(n''_v + \frac{1}{2}\right)^2\right] \tag{2.19}$$

Hence the frequency of vibrations $\nu$ corresponding to a given band is

$$\nu = (n'_v - n''_v)\,\omega - \alpha\omega\left[\left(n'_v + \frac{1}{2}\right)^2 - \left(n''_v + \frac{1}{2}\right)^2\right] \tag{2.20}$$

if $n''_v = 0$, then

$$\nu = n'_v\omega\,[1 - \alpha\,(n'_v + 1)] \tag{2.21}$$

where $n'_v = 1, 2, 3$.

Consequently for HCl

$$\omega (1 - 2\alpha) = 0.867 \times 10^{14}$$
$$2\omega (1 - 3\alpha) = 1.705 \times 10^{14}$$
$$3\omega (1 - 4\alpha) = 2.521 \times 10^{14}$$

Solving two simultaneous equations and taking the mean value of those obtained, we have

$$\omega = 8.96 \times 10^{13} \text{ and } \alpha = 0.016\,18$$

whence

$$D = \frac{8.96 \times 10^{13}}{4 \times 0.016\,18} = 1.384 \times 10^{15}\ \text{s}^{-1}$$

Sometimes the rotational structure of the bands disappears beginning from a wave of a certain length (sometimes suddenly, and sometimes gradually). The bands exist, but have a diffusion nature. Such diffusion bands are sometimes traced up to the zone of continuous absorption in the ultraviolet region of the spectrum. Sometimes the rotational structure of the bands is again restored when approaching the zone of continuous absorption. If we irradiate molecules with light of wavelengths corresponding to the diffusion sections of the bands, we can detect the products of dissociation of the substance being investigated. It was originally assumed that the transition of the molecules to a special active state preceding dissociation and termed *predissociation* corresponds to the appearance of the diffusion bands. Actually, however, as shown by experience and theory, the appearance of the diffusion bands is due to decomposition of a molecule. Notwithstanding this circumstance, the term *predissociation* remained in use, since the mechanism of dissociation of molecules, as will be shown later, differs somewhat from the mechanism of photochemical dissociation considered earlier and connected with the appearance of a continuous absorption zone in the short-wave region of the spectrum. The phenomenon of predissociation is observed not only in diatomic molecules such as $S_2$ and $P_2$, but most frequently in polyatomic molecules, for example of ammonia, acetaldehyde, benzene, pyridine, naphthalene. Thus, for acetaldehyde in the interval from 3484 to 3050 Å the bands become diffusion ones and the rotational structure disappears, although it is still possible to trace about sixty bands. When acetaldehyde is irradiated with light having wavelengths greater than 3050 Å, no decomposition of the acetaldehyde is observed, but when light with a wavelength less than 3050 Å is used, products of dissociation of the acetaldehyde are detected, namely, methane and carbon monoxide.

The disappearance of the rotational structure of the bands is thus explained by the fact that a molecule decomposes during a time that is less than the duration of one revolution, although it has time to complete a considerable number of vibrations (about 100). For this reason quantizing of the vibrational motions remains possible.

Quantum mechanics allows us to develop the theory of predissociation. To understand the phenomenon of predissociation, let us consider the qualitative aspect of this theory. For each given electronic state of a molecule we can construct a system of vibrational levels. Fig. 2.5 *A*, *B* and *C* show vibrational levels corresponding to three electronic states of a molecule. Quantum mechanics shows that there is a finite probability of transition of a system from a discrete level of a system of terms *B* into a zone of continuum of a system of terms *A*, or accordingly from the discrete level of system *B* to the zone of the continuum of system *C* bordering with this level. The transition from the discrete level of one system of levels to the continuous zone of another system of levels is possible when the rules of selection for electron transitions are obeyed (both levels must have

the same value of the total quantum number $I$, i.e. $\Delta I = 0$). The projections of the orbital angular momentum of the electrons onto a line connecting the nuclei should differ by not more than unity, i.e. $\Delta\lambda = 0$ or $\pm 1$, both levels should belong to electronic states of the same multiplicity, i. e. $\Delta S = 0$, they should have the same symmetry for reflection at the origin of coordinates. In molecules consisting of two identical nuclei, both levels should also have the same symmetry relative to their nuclei. In addition, the conditions imposed onto the states of vibration of the nuclei by the Franck-Condon principle must be observed.[1]

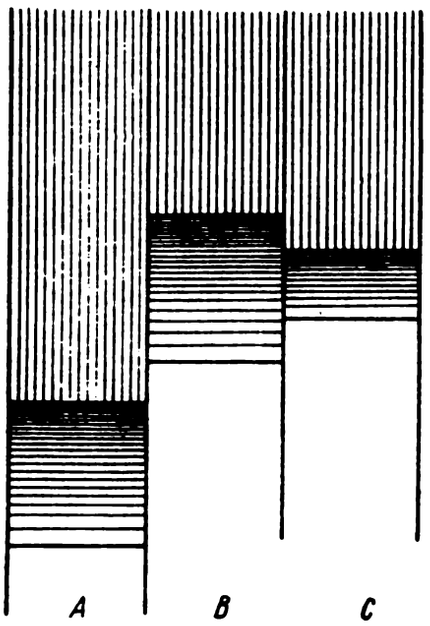


Fig. 2.5. Vibrational levels corresponding to electronic states $A$, $B$ and $C$

For a molecule in the upper vibrational level of an excited electronic state there are two possibilities—either to return to a lower energy level by emitting light, or to pass over to a state when its energy levels will be in a continuum, and as a result the excess energy will be spent to rupture the chemical bond, i.e. dissociation will occur. Thus, if the transition from the discrete system of levels to the continuous one is permitted by the relevant selection rules, the onset of predissociation should be manifested not only in that the rotational structure of the bands will disappear, but also in that the intensity of fluorescence will reduce. The latter can be used for fixing predissociation. This method of establishing predissociation is often more convenient than the detection of the broadening of the rotational lines in the band. For example, in irradiating $NH_3$ with light whose wavelength corresponds to the zone of predissociation, the fluorescence of the ammonia completely disappears, and its decomposition no longer depends on the pressure. These facts indicate unambiguously that dissociation of the ammonia occurs directly after the absorption of light, and not as a result of the additional influence of collisions of molecules with one another. It is the easiest to form a notion of the predissociation process by considering potential curves (Fig. 2.6) and using the Franck-Condon principle. Curve *1* in both cases corresponds to the normal state. As a result of electronic excitation, a molecule transfers to a new energy state which curve *2* corresponds to. Curve *3* corresponds to a still greater store of energy. As long as the upper vibrational level is below level $D$, the molecule is quite stable, and bands of a normal structure correspond to these transitions. Beginning from level $D$ and higher, diffusion bands appear in the spectrum. It is easy to understand their appearance if we consider the behaviour of a molecule whose vibrational energy corresponds to points above level $D$. Assume that upon excitation a molecule gets onto level $E$. The vibrations of the nuclei of a molecule and the changes in the potential

[1] The process of transition of an electron to a higher energy state is completed quite rapidly, so that the relatively heavy nuclei occupy their previous positions at the moment when the transition of the electron is completed. Hence the transition at the first moment after excitation of the molecule is performed from a lower potential curve to the point on an upper potential curve that corresponds to a constant distance between the nuclei, i.e. is above its previous position in the unexcited state. This rule establishing the possibility of transition from a given vibrational level to any other level, first established by J. Franck, was later substantiated from the quantum mechanics viewpoint by F. Condon and was named the Franck-Condon principle.

energy of a molecule can be compared with the motion of a heavy ball. A ball lifted to point $E$ on curve *2* and released will move with a continuously growing velocity and after passing the lowest point of the potential curve with the maximum kinetic energy will rise to point $E'$ at the same level as point $E$. In return motion, when the ball reaches point $C$, it will have two possibilities—either to roll downward along the same curve, or to pass over to curve *3* without changing its kinetic energy (according to the Franck-Condon principle). If it passes over to curve *3*, then moving along it the ball will rise higher than the level $D$ and therefore, returning along the same curve, it will jump out of its limits. Physically this will correspond to the dissociation of a molecule, and the parts of the

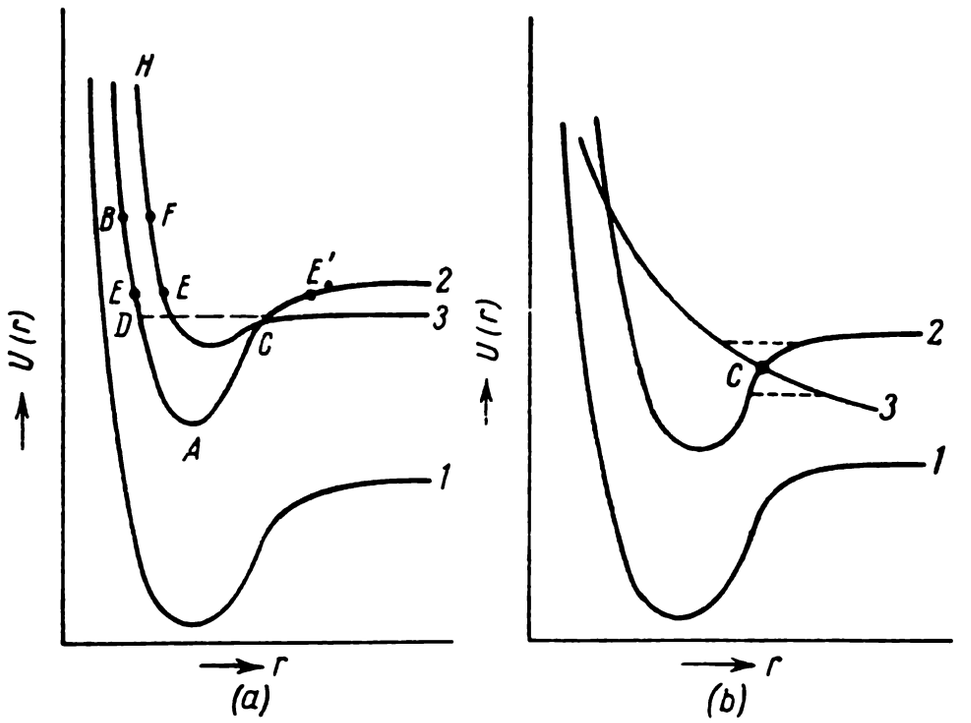


Fig. 2.6. Two cases of the appearance of diffusion bands in spectra:
*a*—all the potential curves correspond to the domination of forces of attraction between the atoms; *b*—curve *3* corresponds to the domination of forces of repulsion between the atoms

molecule will fly apart with a definite kinetic energy. It is obvious that the higher the level which the molecule passes over to in comparison with level $D$, the greater will be the kinetic energy of the fragments of the molecule flying apart. But the higher the level $E$ which the molecule passes over to is above level $D$, the greater is the velocity of the vibrating nuclei when the molecule passes point $C$ of intersection of the potential curves, and therefore the greater is the probability of the molecule " jumping across" this dangerous point and remaining on previous curve *2*. Hence it can be understood that sometimes upon transition to the ultraviolet region of the spectrum the rotational structure of the bands is again restored. In the case under consideration the boundary of predissociation will be sharp.

If curve *3* is a repulsion curve (Fig. 2.6*b*), then transition to curve *3* is also possible below point $C$. This is the so-called *tunnel effect*. Transition is possible between the points of curves *2* and *3* connected by dotted lines. Here broadening of the bands begins before point $C$, i.e. before predissociation begins.

The predissociation of a molecule of nitrogen dioxide is of considerable interest and has been well studied. Here both cases dealt with above are realized, and two predissociation zones are observed. A gradual broadening of the lines in a band is observed at $\lambda = 3800$ Å and then at $\lambda = 2459$ Å (Fig. 2.7). In the first zone a molecule of nitrogen oxide and a normal atom of oxygen appear. The

second zone of predissociation corresponds to the formation of nitrogen oxide and an excited atom of oxygen in the state $^1D_2$. In the zone of predissociation, when fluorescence completely attenuates, photochemical dissociation of a molecule takes place with quantum yield 2. This allows us to assume that the reaction has the following mechanism

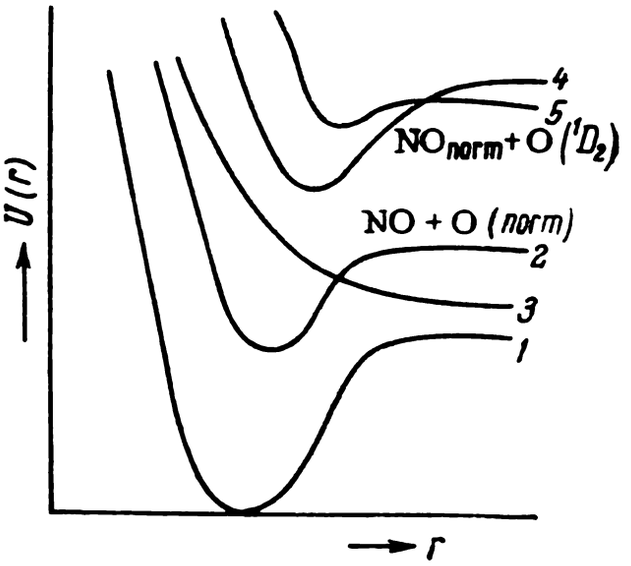


Fig. 2.7. Predissociation of $NO_2$ molecule

$$NO_2 \xrightarrow{+h\nu} NO + O$$

$$NO_2 + O \longrightarrow NO + O_2$$

$$2NO_2 \xrightarrow{+h\nu} 2NO + O_2$$

It follows from the nature of the potential curves and what has been said above of the possibility of the tunnel effect in such cases that it is quite difficult to determine the zone of the first predissociation. The second zone of predissociation, as can be seen from the curves, can be determined exactly. As already indicated, the zone of the second predissociation corresponds to $\lambda = 2459$ Å. A quantum of energy equal to 116.2 kcal/mol corresponds to this wavelength. The energy of excitation of oxygen corresponding to the level $^1D_2$ is 45.4 kcal/mol. Therefore the energy of detaching the first atom of oxygen from a molecule of $NO_2$ is equal to 116.2—45.4 = 70.8 kcal/mol.

These data make it possible to find the energy of dissociation of oxygen into atoms by means of the Hess law. It is known from thermodynamic data that

$$NO_2 \longrightarrow NO + \frac{1}{2} O_2 \ (\Delta H^\circ = 13.5 \text{ kcal})$$

Subtracting this equation from the equation of a photochemical reaction

$$NO_2 \longrightarrow NO + O \ (\Delta H^\circ = 70.8 \text{ kcal})$$

and multiplying the result by two, we get

$$O_2 \longrightarrow O + O \ (\Delta H^\circ = 114.6 \text{ kcal})$$

As already indicated, for the process of predissociation to be possible, the selection rules should be observed. These rules can be violated by placing a molecule in an electric or magnetic field. For example, the fluorescence of iodine vapours excited by the green mercury line can be extinguished by a sufficiently intensive magnetic field. As shown by experiments, and also by the nature of the potential curves, a molecule of iodine dissociates into atoms. In the absence of a magnetic field this process is forbidden by the selection rules. In the presence of a magnetic field, the rule requiring the constancy of the angular momentum ($\Delta I = 0$) is removed, and as a result predissociation becomes possible. Such a phenomenon is called *magnetic quenching of fluorescence*. Foreign atoms can also remove the conditions of forbiddenness. For example, molecules of $I_2$ spontaneously dissociate in the presence of atoms of oxygen or argon when irradiated with light having frequencies from the zone of the discrete absorption spectrum ($\lambda = 5100$ Å). This phenomenon is called *induced predissociation*. It has been discovered for the molecular gases $I_2$, $Br_2$, $Tl_2$, $S_2$ and the gases $N_2$ and NO. In the

general form this process can be written as

$$AB^{\star} + X = A + B + X$$

where the star indicates the excited state of a molecule or atom.

The phenomenon of predissociation is of very great interest in conducting photochemical reactions, since even a small amount of energy (less than corresponds to the continuous absorption zone) can cause the decomposition of a molecule into atoms. Of special interest in this respect is induced predissociation.

Elementary photochemical processes can be classified into processes of two types:

1. The primary electronic excitation of a molecule that decomposes or changes upon a subsequent collision.
2. Spontaneous photochemical dissociation.

When molecules are illuminated by light whose frequencies correspond to the discrete zone of absorption, processes of the first type are possible, and when they are illuminated by light whose frequencies correspond to the continuous zone of the spectrum, processes of the second type are possible.

Dissociation is sometimes observed when photochemically excited molecules collide with unexcited molecules of a different species. This process obviously occurs owing to the transfer of energy (in collision) by the excited molecules to unexcited molecules. If the energy transferred is greater than that of dissociation, the molecules decompose. The transfer of the excitation energy to other molecules is called a *collision of the second kind*. The process of dissociation as a result of such a collision has been termed *sensitized dissociation*. This phenomenon was discovered when the appearance of hydrogen atoms was observed in a mixture of mercury and hydrogen irradiated with light of a wavelength corresponding to the line of mercury excitation. This process can be depicted schematically as follows:

$$Hg \xrightarrow{+h\nu} Hg^{\star}$$

$$H_2 + Hg^{\star} \longrightarrow H + H + Hg$$

This process is quite verisimilar, since the dissociation energy of hydrogen molecules is equal to 4.4 eV, and the first level of excitation of mercury corresponds to an energy of 4.9 eV.

In investigating the synthesis of ammonia in a silent electric discharge, it was discovered that the process accelerates in the presence of mercury vapour. This was found to be explained by the sensitized dissociation of hydrogen in the presence of mercury according to the mechanism considered above, and also by the reaction

$$N_2^{\star} + H_2 \longrightarrow H + H + N_2$$

The formation of a great number of hydrogen atoms as a result of this reaction accelerates the process of synthesis of ammonia, since the hydrogen atoms participate in the intermediate stages of synthesis.

**2.3. Dissociation of Molecules upon Electron or Ion Collision.** Below we shall consider several aspects of such dissociation.

*Exchange of Kinetic Energies in an Elastic Collision.* The quantities of energy exchanged by particles can easily be computed on the basis of the laws of conservation of momentum and energy. As a result of a collision, atoms and molecules may become ionized, and molecules may dissociate into atoms.

Let us first consider the exchange of kinetic energies between elastic particles in a central collision. Let $m_1$ be the mass of the first particle, $v_1$ its velocity before the collision, $u_1$ its velocity after the collision, $m_2$ the mass of the second particle, $v_2$ its velocity before the collision and $u_2$ its velocity after the collision. According to the law of conservation of energy, the sum of the kinetic energies of the particles before the collision is equal to the relevant sum after the collision, i.e.

$$m_1v_1^2 + m_2v_2^2 = m_1u_1^2 + m_2u_2^2 \tag{2.22}$$

According to the law of conservation of momentum, the sums of the momenta before and after the collision should also be equal, hence

$$m_1v_1 + m_2v_2 = m_1u_1 + m_2u_2 \tag{2.23}$$

The fraction $\alpha$ of the energy of the first particle transmitted to the second particle upon collision is equal to

$$\alpha = \frac{m_2u_2^2 - m_2v_2^2}{m_1v_1^2} = \frac{m_1v_1^2 - m_1u_1^2}{m_1v_1^2} = 1 - \left(\frac{u_1}{v_1}\right)^2 \tag{2.24}$$

The quantity $\alpha$ can be expressed through the initial velocities of the particles as follows. Equations (2.22) and (2.23) can be rewritten as follows:

$$\left.\begin{aligned} m_1(v_1^2 - u_1^2) &= m_2(u_2^2 - v_2^2) \\ m_1(v_1 - u_1) &= m_2(u_2 - v_2) \end{aligned}\right\} \tag{2.25}$$

Dividing the upper equation by the lower one, we get

$$v_1 + u_1 = v_2 + u_2 \tag{2.26}$$

Multiplying Eq. (2.26) by $m_2$ and subtracting the expression obtained from Eq. (2.23), we get

$$m_1v_1 + m_2v_2 - m_2v_1 - m_2u_1 = m_1u_1 - m_2u_2 \tag{2.27}$$

whence

$$u_1 = \frac{2m_2v_2 + (m_1 - m_2)v_1}{m_1 + m_2} \tag{2.28}$$

Inserting Eq. (2.28) into Eq. (2.24), we have

$$\alpha = 1 - \left[\frac{(m_1 - m_2) + 2m_2\frac{v_2}{v_1}}{m_1 + m_2}\right]^2 \tag{2.29}$$

If we assume that the velocity of the second particle $v_2 = 0$, then

$$\alpha = \frac{4m_1m_2}{(m_1+m_2)^2} \tag{2.30}$$

If $m_1 = m_2$, then $\alpha = 1$, i.e. the entire energy of the first particle will be transferred to the second one. If $m_1 \ll m_2$, then neglecting the value of $m_1$ in the denominator of Eq. (2.30), we get

$$\alpha = \frac{4m_1}{m_2} \tag{2.31}$$

Let us assume that the first particle is an electron and the second one a hydrogen molecule. Since the mass of a hydrogen atom is 1849 times greater than that of an electron, we have

$$\alpha = \frac{4 \times 1}{2 \times 1849} \cong 0.001$$

i.e. the quantity of energy transmitted will be very small. After the collision the electron will change the direction of its motion, almost completely retaining its previous velocity.

Upon collision an electron cannot transfer its kinetic energy to a molecule and increase the rotational or vibrational energy of the latter since the mass of an electron is very small. For conversion of the kinetic energy of translational motion of an electron into the vibrational energy of a molecule, a collision along the axis of the latter is the most advantageous. But owing to the unfavourable ratio of the masses, even in such a collision only a small fraction of the kinetic energy of the electron, as already shown above, can be transferred to the molecule. Despite this fact, in certain circumstances the transfer of the kinetic energy of translational motion of the electron into vibrational energy of the molecule it collides with is possible. The electron can so change the internal field of the molecule with its electric field that the vibrational state of the molecule will change. Experiments show that electrons having an energy of 5 eV excite vibrational quanta of nitrogen and carbon monoxide molecules, the rotational motion of the molecules not changing. If we assume that only the first vibrational quanta are excited, then calculations show that the probability of nitrogen being excited is equal to 1/110, and of carbon monoxide 1/30. The magnitudes of the vibrational quanta of these molecules are almost the same. The difference between the probabilities of excitation of these molecules is explained by the fact that a molecule of carbon monoxide has its own dipole moment, which increases its interaction with an electron.

*Conversion of Kinetic Energy of Translational Motion of an Electron into Energy of Electronic Excitation of an Atom or Molecule.* On the basis of classical notions, such an energy-transfer process can

be considered as an inelastic collision. A collision in which translational energy is converted into internal energy is an inelastic one. In an inelastic collision the deformation of the colliding bodies increases until their velocities become the same (i.e. $u_1 = u_2 = u$), after which the bodies will stop pressing on each other and will move together.

According to the law of conservation of momentum

$$m_1v_1 + m_2v_2 = (m_1 + m_2)\,u \tag{2.32}$$

whence

$$u = \frac{m_1v_1 + m_2v_2}{m_1 + m_2} \tag{2.33}$$

The momentum exchanged by the bodies

$$\bar{p} = m_1v_1 - m_1u = m_2u - m_2v_2 \tag{2.34}$$

The change in the kinetic energy in an inelastic collision is

$$I = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 - \left(\frac{1}{2}m_1u^2 + \frac{1}{2}m_2u^2\right) \tag{2.35}$$

Insertion of Eq. (2.33) into Eq. (2.35) yields

$$I = \frac{1}{2}\frac{m_1m_2}{m_1 + m_2}(v_1 - v_2)^2 \tag{2.36}$$

The fraction $\beta$ of the kinetic energy converting into internal energy of the molecule (the energy of electronic excitation) is

$$\beta = \frac{I}{E_k} \leqslant \frac{\dfrac{m_1m_2}{m_1 + m_2}(v_1 - v_2)^2}{m_1v_1^2 + m_2v_2^2} \tag{2.37}$$

The equality sign corresponds to a central collision. In an off-centre collision (the sign $<$) the fraction of the energy transferred is less than in a central one. If the velocity of the particle being struck $v_2 = 0$, then

$$\beta \leqslant \frac{m_2}{m_1 + m_2} \tag{2.38}$$

and if the first particle is an electron and the second one a molecule, then $m_1 \ll m_2$. Consequently, in an inelastic collision $\beta = 1$, i.e. all the energy of the electron can completely change into the energy of electronic excitation of an atom or molecule. Experiments show that such a conversion obeys quantum laws. It is possible only when the energy of the colliding electron is equal to the energy that is required for the transition of an electron in a molecule from the given state to any other one permitted by the quantum conditions of selection. Collisions between electrons and atoms or molecules leading to the excitation of the atoms or molecules at the expense

of the kinetic energy of the electrons are called *collisions of the first kind*. J. Franck and H. Hertz investigated collisions of electrons with atoms, and on the basis of the results of these investigations worked out convenient methods for determining the resonance, critical and ionization potentials of atoms.

The excitation, or ionization, of atoms when they collide with electrons depends on the energy or velocity of the latter. In the majority of cases the probability of excitation of a molecule or an atom to the corresponding energy level grows with an increase in the velocity of the electrons to a definite value, and with a further increase in the velocity of the electrons the probability of excitation diminishes. By the *probability of excitation* is meant the ratio between the number of collisions of an electron with an atom or molecule leading to excitation and the total number of collisions. Curves showing the dependence of the probability of excitation on the velocity of electrons are called *excitation function curves*. The position of the maximum on such a curve depends on the multiplicity of the initial and excited levels (terms). Upon the excitation of terms of the same multiplicity as the initial term of an atom, the excitation function grows quite slowly, reaching its maximum value at very great velocities of the electrons. The velocity of the electrons in these cases is usually several times greater than the minimum value of the velocity of an electron at which excitation of an atom is possible. If upon collision with an electron a term of a different multiplicity than the initial one is excited, the excitation function rapidly reaches a maximum and then just as rapidly decreases (Fig. 2.8). The excitation function for two close mercury lines is shown in Fig. 2.8. Upon excitation of the line 2655 Å the mercury atom passes from the normal state $1^1S_0$ to the state $4^1D_2$. The multiplicity does not change. After a certain time the excited atom undergoes transition from the excited state $4^1D_2$ to the state $2^3P_1$, emitting light having a wavelength of 2655 Å. Excitation of the second line leads to a transition from the state $1^1S_0$ to the state $4^3D_1$. A change in the spin, the so-called *intercombination*, occurs, in which the striking and the struck electrons change places. A definite time is required for such an exchange, therefore at low velocities of an electron such a transition is possible, while at high velocities it becomes difficult.

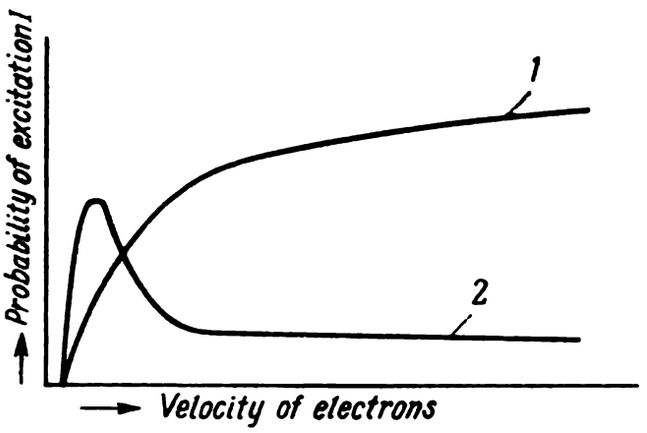


Fig. 2.8. Excitation function for two close mercury lines:

*1*—the multiplicities of the initial and excited terms are the same; *2*—they are different

The value of the excitation probability appreciably depends on the nature of the atoms and terms in them. The exciting action of an electron collision is more effective than the action of light. This is explained by the fact that the electric field of the electron removes the forbiddenness of the transitions. For example, the rule of retaining the multiplicity $\Delta S = 0$ when a molecule is bombarded with electrons is replaced by the less rigid rule $\Delta S = 0, \pm 1$.

This rule is obtained as a consequence of the possibility of colliding electrons exchanging places, owing to which the electron spin may either remain the same or change by $\pm 1$. The probability of ionization upon an electron collision is maximum at an energy of the electrons ranging from 100 to 200 eV and is usually equal to several tenths.

Different processes of ionization and dissociation are probable when a molecule is bombarded with electrons. To date there is no theory that would make it possible to calculate the probability of a process of excitation of a molecule or its decomposition. The collision of electrons having a low energy with molecules usually leads to the transition of the latter to higher rotational, vibrational or electronic energy levels. With an increase in the velocity of the electrons, a moment sets in when the energy of the colliding electron is sufficient for ionization of a molecule. With a further increase in the energy of the electrons, excitation of an ionized molecule may lead to dissociation, as a result of which ions with a lower mass and also neutral fragments of the molecule appear. The potential corresponding to the lowest energy of an electron at which upon collision with a molecule the latter dissociates with the formation of ions is called the *appearance potential.*

This energy is equal to the sum of the bond breaking energy, the dissociation energy of the ionized molecule fragment formed, the kinetic energy and the excitation energy of all the molecule fragments formed. Expressed in electron-volts, it is numerically equal to the appearance potential expressed in volts.

The appearance potentials of selected ions in methane are given below:

| Reaction | Appearance potential, V |
|---|---|
| $CH_4 \rightarrow CH_4^+$ | 13.1 |
| $CH_4 \rightarrow CH_3^+ + H$ | 14.4 |
| $CH_4 \rightarrow CH_2^+ + H_2$ | 15.7 |
| $CH_4 \rightarrow H^+ + CH_2 + H$ | 22.7 |
| $CH_4 \rightarrow CH^+ + 3H$ | 23.3 |
| $CH_4 \rightarrow H^+ + C + 3H$ | 29.4 |

Dissociation of a molecule upon an electron collision usually directly follows excitation and is similar to the process of photochemical dissociation considered in Sec. 2.2. In both cases the molecule passes over either onto the repulsion curve or to such a region on the curve of stable excitation in which the energy of the molecule is greater than the energy of dissociation into the corresponding products.

It is interesting to note that the introduction of isotope atoms into a molecule frequently leads to a considerable change in the probability of bond breaking in bombardment with electrons. For example, the C—D bond in methane, ethane and propane is weaker than the C—H bond in the same molecules. In addition, isotope substitution in general leads to the weakening of C—H bonds adjacent to a C—D one. The probability of breaking of the $^{12}C—^{12}C$ bond is greater by 20% than that of breaking of the $^{12}C—^{13}C$ one.

Let us consider the calculation of the bond energy according to the appearance potential. When propane is bombarded with electrons, the appearance potential of the ion $C_2H_5^+$ is equal to 14.5 V, or

$$C_3H_8 = C_2H_5^+ + CH_3 \quad (\Delta H^\circ = 14.5 \text{ eV})$$

The energy of this reaction should be equal to the sum of the bond dissociation energy $D_{CH_3-C_2H_5}$ and the energy of ionization of the radical $C_2H_5^\cdot$. The appearance potential of the ion $C_2H_5^+$ in the dissociation of ethane is equal to 15.2 V, or

$$C_2H_5^+ + H = C_2H_6 \quad (\Delta H^\circ = -15.2 \text{ eV})$$

The appearance potential in this case is numerically equal to the sum of the bond dissociation energy $D_{C_2H_5-H}$ and the energy of ionization $I_{C_2H_5}$ of the radical $C_2H_5^\cdot$. Thermochemical data give

$$CH_4 + C_2H_6 = C_3H_8 + 2H \quad (\Delta H^\circ = 5.08 \text{ eV})$$

Summation of these equations yields

$$CH_4 = CH_3^\cdot + H \quad (\Delta H^\circ = 4.38 \text{ eV})$$

i.e.

$$D_{CH_3-H} = 4.38 \text{ eV}$$

The value of the C—H bond energy obtained is authentic with an accuracy up to $\pm 0.2$ eV and corresponds to the value 101 $\pm$ 4.5 kcal/mol. This value is close to the value 103 kcal/mol calculated theoretically, and also approximately corresponds to the mean value of the bond energy found by the kinetic and photochemical methods, which give the values 108 and 94.8 kcal/mol, respectively.

When molecules are bombarded with electrons, the appearance of not only positive, but also of negative ions is observed. Thus, when methane is bombarded with electrons, the ions $CH_2^-$, $CH^-$, $C^-$ and $H^-$ appear. The joining of electrons to molecules, radicals or atoms is due to their having affinity for an electron. When negative ions are formed, the energy liberated as a result of the picking up of an electron very frequently exceeds the energy of dissociation of a molecule. For example, the following process is observed for halogens:

$$e + X_2 \rightarrow X^- + X$$

where X is a halogen.

A similar process proceeds with the participation of hydrogen halides:

$$e + HCl \rightarrow Cl^- + H$$

The formation of negative ions is observed in many gases (for example, in $NH_3$, $N_2O$, $SO_2$, $H_2S$, $H_2O$), the ions $NH^-$, $O^-$, $SO^-$, $HS^-$ and $HO^-$ being formed.

When electrons collide with excited molecules, the transfer of the energy of excitation of a molecule to an electron is possible, as a result of which the passing over of the molecule to the normal state is not accompanied by radiation (a collision of the second kind).

*Ionization of Molecules by Collision with an Atom or Ion.* The fraction of the kinetic energy changing into internal energy, as already indicated, is determined by the expression

$$\frac{I}{T} \leqslant \frac{m_2}{m_1+m_2}$$

If $m_1 \approx m_2$, we have

$$E_k \geqslant 2I \tag{2.39}$$

i.e. the kinetic energy of the striking particle must be approximately two times greater than the energy of excitation. Experimental data confirm this conclusion. Indeed, when atoms are ionized by atoms, the energy at which a quick atom can ionize an atom of the same gas somewhat exceeds the double energy of ionization. This can be seen from Table 2.1.

TABLE 2.1

**Ionization Energy of Inert Gas Atoms**

| Atoms | Double ionization energy $2I$, eV | Energy of striking atom, eV |
|---|---|---|
| He | 49 | 60 |
| Ne | 43 | 60 |
| Ar | 31 | 40 |

With an increase in the energy of the striking atom, the probability of ionization increases, and the heavier an atom, the higher is its ionization ability. Thus, when the energy of the striking atom is 100 eV, one atom of argon ionizes on the average about two atoms of Ar, 10 atoms of Ne—approximately one atom of Ne, and 100 atoms of He ionize one atom of He. When atoms are ionized by ions these relations change somewhat. The striking ion must overcome the repulsion appearing as a result of ionization of the atom. Here the energy of the striking ion can approximately be represented as the sum

$$E = 2\,(I + E_p) \tag{2.40}$$

where $E_p$ = potential energy of two ions equal to $\frac{e^2}{r_1+r_2}$ ($r_1$ and $r_2$ are the radii of the ionizing and the newly appearing ion)

$I$ = ionization potential.

The factor 2 holds only for ions whose masses are approximately identical. It has been found experimentally that ions of argon $Ar^+$ begin to ionize atoms of Ar when they reach a velocity corres-

ponding to an energy of 330 eV. Ionization of atoms of He and Ne becomes noticeable only when the velocity of the striking ions $He^+$ and $Ne^+$ corresponds to an energy greater than 500 eV. In collision excitation of atoms and molecules, the potential of excitation by ions is much higher than that by electrons.

**2.4. Thermal Dissociation.** Thermal dissociation of molecules occurs either as a result of absorption of infrared radiation by them, or as a result of collision of molecules. The dissociation of molecules as a result of absorption of infrared radiation does not differ in principle in any way from photochemical dissociation.

In the dissociation of molecules caused by their colliding, the main part is played by the vibrational and partly by the rotational energy of the molecules. If as a result of a collision of molecules the vibrational energy of one of them grows, such a molecule upon subsequent collisions may pass over either into a state with a lower store of vibrational energy, or into a state with a still greater store of such energy. Usually one collision results in the transfer of one vibrational quantum. The probability of transferring vibrational quanta by collisions rapidly grows with the temperature. If upon collisions the vibrational energy of a diatomic molecule corresponds to the vibrational quantum number $n_{v,\,max} - 1$, the following collision will lead to dissociation of this molecule, which can be depicted as follows:

$$X_{2(n_{v,\,max}-1)} + X_2 \longrightarrow [X_{2(n_{v,\,max})} X_2] \longrightarrow X + X + X_2$$

where the expression in brackets characterizes the state at the moment of collision.

In complicated molecules the vibrational energy accumulates along all the bonds, and for this reason the total vibrational energy may exceed the dissociation energy. This accumulated vibrational energy, migrating inside a molecule, may concentrate on one of the bonds, which will lead to decomposition of the molecule. If the duration of concentration of the energy on a definite bond is commensurable with the interval between collisions, the reaction of thermal dissociation proceeds according to the bimolecular law. If the time required for the concentration of the vibrational energy on one bond is greater than the interval between two collisions, the molecule will decompose when a certain time elapses after the collision, and dissociation will proceed according to the mechanism of a monomolecular reaction.

The rotational energy also plays a certain part in the process of thermal dissociation of molecules:

$$E_r = \frac{I\omega^2}{2} \tag{2.41}$$

where $I$ = moment of inertia of a molecule
$\omega$ = angular velocity.

Inserting into Eq. (2.41) the value of the moment of inertia

$$I = \mu r^2 \tag{2.42}$$

where $\mu$ = reduced mass of a diatomic molecule
$r$ = internuclear distance,
and multiplying the numerator and denominator by $\mu r^2$, we get

$$E_r = \frac{\mu^2 r^2 r^2 \omega^2}{2\mu r^2} \tag{2.43}$$

But $r\omega = v$ is the linear velocity of rotation, therefore Eq. (2.43) can be written as follows:

$$E_r = \frac{\mu^2 v^2 r^2}{2\mu r^2} \tag{2.44}$$

Taking into account that $\mu\omega r = P$ (where $P$ is the impulse of rotation), we get

$$E_r = \frac{P^2}{2\mu r^2} \tag{2.45}$$

It is known from the quantum theory of a molecule that the rotational energy of a molecule can be expressed as follows:

$$E_r = \frac{h^2}{8\pi^2 I} n_r (n_r + 1) \tag{2.46}$$

where $h$ = Planck constant
$n_r$ = rotational quantum number.

The internal energy $U(r)$ of a molecule will be the sum of the potential energy $E_p(r)$ and the rotational energy $E_r$, i.e.

$$U(r) = E_p(r) + \frac{P^2}{2\mu r^2} \tag{2.47}$$

Let us differentiate this expression. We get

$$U'(r) = -f(r) = \frac{dE_p(r)}{dr} - \frac{P^2}{\mu r^3} \tag{2.48}$$

where $f(r)$ is the force of interaction of the atoms.

It can be seen from the last equation, with account taken of Eqs. (2.45) and (2.46), that at a great value of $n_r$ the centrifugal force $P^2/\mu r^3$ can be considered greater than $dE_p(r)/dr$, i.e. the force $f(r)$ will be positive. In other words, the forces of repulsion will be greater than those of attraction, and the molecule will decompose.

If the dependence of the internal energy on the internuclear distance for different values of $n_r$ is represented graphically, we get a family of curves (Fig. 2.9). All these curves tend to one asymptote at great values of $r$. When going over to small values of $r$, in contrast to the potential curves for a non-rotating molecule, these curves first pass through a maximum, and then through a minimum corresponding to a stable state. Here the ordinates of each point of the curve are equal to the sum of the potential $E_p(r)$ and the kinetic $E_r$ energies. At a certain rotational quantum number the maximum and minimum of the curve disappear, and a point of inflection appears. The following curve will have neither a maximum nor a minimum, i.e. it will be a repulsion curve.

The decomposition of a molecule caused only by an increase in its rotational energy has been established for HgH. In the line and band spectrum of emission of HgH at a rotational quantum number equal to 31 the band terminates. This indicates decomposition of the molecule of HgH upon its transition to a rotational energy level determined by the number 31. With the simultaneous excitation of vibrations, the molecule decomposes at smaller maximum values of the number $n_r$. For a molecule in the vibrational quantum state $n_v'' = 1$, the value of $n_r$ corresponding to dissociation is 24, for $n_v'' = 2$ we have $n_r = 17$ and for $n_v'' = 3$ the rotational quantum number $n_r = 8$. Hence the conclusion can be made that the rotational energy when added to the vibrational energy may have an appreciable influence on the thermal decomposition of molecules.

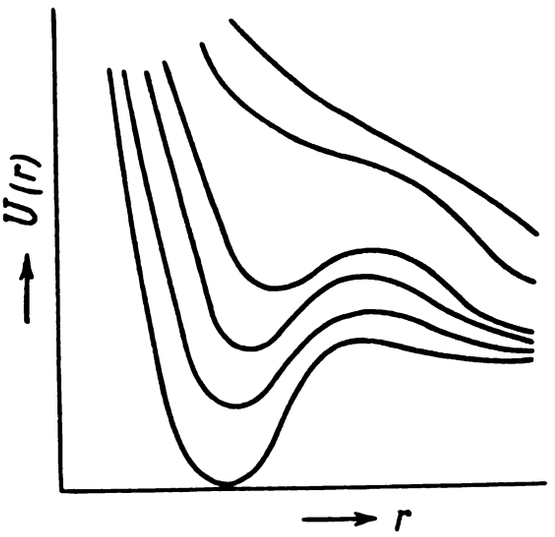

Fig. 2.9. Dependence of internal energy of diatomic molecule on internuclear distance

**2.5. Dissociation of Molecules on Solid Surfaces.** The presence of a solid surface quite frequently facilitates dissociation. Cases are known when active centres of a reaction—atoms or radicals—appear on a surface and then initiate reactions proceeding in the bulk. For example, if jets of hydrogen and oxygen heated to 520 °C are directed onto each other, no reaction will take place; it becomes possible to initiate a reaction only at a temperature of the gases exceeding 560 °C. If a quartz rod heated to 520 °C is introduced into the intersection of the hydrogen and oxygen jets, however, an explosion will occur. Obviously active centres of the reaction appear on the surface of the solid, and, passing into the bulk, initiate a reaction in it.

The dissociation of molecules on heated surfaces may be due to (1) the transfer of the energy of electronic excitation of the surface atoms and molecules to the molecules colliding against the surface, and (2) the reduction in the energy of dissociation of the adsorbed molecules into atoms.

If dissociation of molecules into atoms is due to the first reason, it is similar to the process of induced dissociation already considered. The possibility of such a process of energy transfer is confirmed by the extinguishing of the fluorescence of pigments adsorbed on the surface of solids by oxygen. The dissociation of halogen molecules on heated solid surfaces apparently occurs under the influence of a similar action of the surface.

The dissociation of molecules on a surface is sometimes a typical heterogeneous process and is due to the fact that, as can easily be shown, the dissociation energy of the molecules adsorbed on a surface is lower than the dissociation energy of the same molecules in the bulk.

The heat of dissociation $Q_d$ of a diatomic molecule in a gas is usually approximately equal to 100 kcal/mol, the heat of adsorption of a molecule $q_a \approx 10$ kcal/mol, and the heat of adsorption $Q_a$ of an atom is approximately equal to 35 kcal/g-atom. Using Hess's law, we can so combine these three quantities as to obtain the quantity $Q_{d,s}$ interesting us, i.e. the heat of dissociation of a molecule on the surface. The reaction of formation of a molecule in the bulk can be written as

$$2X = X_2 + Q_d$$

If we denote the surface by $S$, the process of adsorption of a molecule on the surface can be written as follows:

$$X_2 + S = X_2(S) + q_a$$

where $X_2(S)$ is a molecule adsorbed on surface $S$.

The process of adsorption of two atoms on surface $S$ can be written as

$$2X + S = 2X(S) + 2Q_a$$

Subtracting the third reaction from the sum of the first two, we get

$$2X(S) = X_2(S) + Q_d + q_a - 2Q_a$$

Obviously, the quantity interesting us will be

$$Q_{d,s} = Q_d + q_a - 2Q_a$$

If we substitute for the quantities in the last equation their values given above, we have

$$Q_{d,s} = 100 + 10 - 2 \times 35 = 40 \text{ kcal/mol}$$

Thus the heat of dissociation of an adsorbed molecule is much less than the heat of dissociation of a molecule in the bulk. If we assume that the energy of activation of the dissociation process is close to the energy of dissociation, the rate of dissociation of molecules on surfaces will be higher than that in the bulk. The surface will play the part of a catalyst. But a catalyst does not shift the position of equilibrium, consequently the concentration of the atoms in the bulk, regardless of whether there is a surface or not, will be the same. If a process connected with the consumption of atoms is possible in the bulk, then in the presence of a surface this process will proceed more rapidly than a purely bulk process.

**2.6. Free Atoms and Radicals.** Free atoms and radicals play a great part in many chemical processes. In a number of cases they are the active centres that stimulate a chemical process. This relates, in particular, to chain reactions. Radicals differ from molecules in having one or more free valences. It is this factor that frequently explains their high reaction ability.

Free radicals can be obtained in different ways: (1) by thermal decomposition of metallo-organic or organic compounds; (2) by the photochemical decomposition of aldehydes and ketones; (3) as a result of a reaction in an electric discharge; (4) by the action of metals on organic halogen derivatives; and (5) by bombarding molecules with $\alpha$-, $\beta$-, $\gamma$-rays and neutrons.

The breaking of a covalent bond in molecules of a gas usually leads to the formation of two neutral radicals. Such reactions are called *atomic* or *homolytic* ones. The breaking of a covalent bond in a molecule may also lead to the formation of two oppositely charged ions. Such reactions are called *heterolytic* ones and are almost never observed in gases, but are very characteristic of solutions. The explanation is that heterolytic decomposition in gases requires the expenditure of a large quantity of energy to overcome the mutual electrostatic attraction of the ions. In solutions, on the other hand, the great permittivity of many solvents appreciably reduces the electrostatic attraction of ions, and consequently the energy of heterolytic breaking of a covalent bond may become less than the energy of homolytic breaking of it. In addition, heterolytic decomposition is facilitated by polarization of the dissociating bond under the action of the electric fields of the polar solvent molecules.

Heterolytic decomposition proceeds the easier, the greater is the electrical asymmetry of the bond being broken. Homolytic breaking of covalent bonds in solutions is observed only if the solvent has a low permittivity, when the reacting bonds are only slightly polar (for example, C—C, C—H, C—N). With highly polar bonds, such as O—H, N—H and C—Cl, heterolytic decomposition is usually observed even if the solvent has a low permittivity.

Free organic radicals generally have an uncompensated electron spin, and therefore they display paramagnetic properties. Paramagnetism can be considered as an indicator of free radicals.

Owing to radicals having free valences, the activation energy of processes proceeding with their participation has the order of magnitude of the activation energy of atomic reactions, and, consequently, they take place at the same high rate as reactions which atoms participate in. Of special interest are radicals having two free valences. The latter include the bivalent atoms O, S, Se and the methylene radical $CH_2^{\cdot}$ formed in the thermal or photochemical decomposition of diazo methane ($CH_2N_2 \rightarrow CH_2^{\cdot} + N_2$) or the photochemical decomposition of ketene ($CH_2{=}CO \rightarrow CH_2^{\cdot} + CO$). Stable organic biradicals can be obtained by detaching two hydrogen atoms from hydrocarbon molecules. Active biradicals are of great significance in chemical processes, since they give rise to the so-called branching chain reactions.

**2.7. Formation of Molecules from Atoms or Radicals.** A stable molecule may form upon collision of two atoms or radicals only if a certain amount of energy not less than the total kinetic energy of the colliding particles is lost as a result of radiation or upon collision with a third particle (the part of which may also be played by the surface of a solid). If there is no loss of energy, the molecule appearing as a result of the collision will decompose after one vibration, since the energy liberated in the formation of the bond remains in the appearing molecule, and it is sufficient to break this bond. In addition, the newly formed molecule will also have the kinetic energy of the colliding particles, which after breaking of the bond will again convert into the kinetic energy of translational motion of the fragments (atoms or radicals) formed.

As already indicated, two mechanisms of stabilization of the newly formed molecule are possible, namely, (1) stabilization by radiation, and (2) stabilization by collision with a third particle (a *triple collision*).

It can be shown that the stabilization of a molecule appearing upon collision of atoms or radicals by radiation is a process with a low probability.

Let us see how real is the process of stabilization of a molecule by radiation connected with a vibrational and electron transitions. For such stabilization the presence of combining levels is necessary first of all. A molecule constructed of two identical atoms cannot in general radiate electromagnetic vibrations owing to the absence of electric charges. Consequently, in this case there are no combining rotational and vibrational levels. Only in molecules constructed of atoms having different masses do combining vibrational levels appear. The possibility of stabilization of a molecule appearing in this case is easy to determine by comparing the duration of collisions $\tau$ with the lifetime of an excited molecule $\tau_0$. It is obvious that for the process of stabilization to be possible, both quantities $\tau$ and $\tau_0$ must be of the same order. The possibility of stabilization of a molecule by radiation is characterized by the quantity

$$\gamma = \frac{\tau}{\tau_0} \tag{2.49}$$

The duration of a collision can be determined as

$$\tau = \frac{2d}{v} \tag{2.50}$$

where $d$ = distance travelled by one atom in the field of another one
$v$ = mean relative velocity of an atom.

Assuming that $d = 2 \times 10^{-8}$ cm and $v = 5 \times 10^4$ cm/s, we get $\tau \approx 10^{-12}$ s.

The mean lifetime of a vibrationally excited molecule can approximately be appraised as the duration of attenuation of a classical vibrator

$$\tau_0 = \frac{3}{8\pi^2} \frac{c\mu}{e^{*2}} \lambda^2 \tag{2.51}$$

where $c$ = velocity of light
$\mu$ = reduced mass of a molecule
$\lambda$ = length of radiated wave

$e^*$ = effective charge equal to $p/r_0$ ($p$ is the dipole moment and $r_0$ the equilibrium distance between the atoms in a molecule).

For a molecule of HCl we have $\lambda = 3.52 \times 10^{-4}$ cm; $p = 1.03 \times 10^{-18}$ cgse and $r_0 = 1.282 \times 10^{-8}$ cm. Hence $\tau_0 \approx 0.035$ s $\approx 10^{-2}$ s and $\gamma = 10^{-10}$, i.e. the difference between $\tau$ and $\tau_0$ is so great that stabilization of a molecule of HCl by radiation of a vibrational quantum is practically impossible. Stabilization of a molecule by radiation connected with an electron transition has a greater probability than the process considered above, but it is also not great. It is known that the lifetime of an electron excited atom or molecule $\tau_0 \approx 10^{-8}$ s, and since the duration of a collision $\tau \approx 10^{-12}$ s, the value of $\gamma$ is equal to $10^{-4}$.

The most probable is stabilization by a triple collision:

$$A + B + M \rightarrow AB + M$$

where M is the third particle.

The probability of stabilization is the greater, the more the degrees of freedom that the third particle has. For example, the stabilization of a molecule of hydrogen by the process

$$H + H + H_2 \rightarrow H_2 + H_2$$

is more effective than as a result of the simultaneous collision of three atoms, namely,

$$H + H + H \rightarrow H_2 + H$$

A solid may be considered as a particle with an enormous number of degrees of freedom, therefore the collision of particles with a surface is especially effective with respect to the dissipation of energy and stabilization of the appearing molecule. A surface, as we have seen, may be the place where the process of dissociation of molecules is easier to accomplish, the result being that active particles (atoms and radicals) are generated on it. But a surface may also play the part of an inhibitor, i.e. facilitate the perishing of atoms and radicals.

There may be two mechanisms in the recombination of atoms on surfaces. The simplest way is the simultaneous collision of two atoms on a surface, which can schematically be written as follows:

$$A + A + S \rightarrow A_2 + S$$

The liberated energy is transferred to the surface and heats the solid. When the number of recombining atoms is great, the surface becomes greatly heated. An example is the heating of solids to high temperatures when atoms of hydrogen recombine on their surface (atomic-hydrogen welding).

The rate of recombination of the atoms depends in a number of cases on the nature of the substance forming the surface. It has been established, for example, that the rate of recombination of hydrogen atoms on different surfaces diminishes in the following order: Pt, Pd, W, Fe, Cr, Ag, Cu, Pb.

The process of recombination of atoms on the surface of a solid is sometimes a typical heterogeneous one. This appears in that the rate of recombination appreciably depends on the chemical nature of the surface. For example, the presence of a monolayer of water on the surface of quartz or glass considerably hinders the recombination of hydrogen and oxygen atoms, and alkali metal halides hamper the recombination of chlorine atoms. The temperature dependence of the rate of recombination of the atoms also indicates the heterogeneous nature of the process. A reduction of the surface temperature frequently facilitates recombination (for example, the recombination of hydrogen atoms accelerates with a reduction in the temperature).

The first stage of a heterogeneous process of recombination is the adsorption of atoms on the surface. The number of adsorbed atoms depends on the nature of the surface and the temperature. Atoms in a gaseous phase collide with atoms adsorbed on the surface, react with them and form molecules. The final, third stage of such a process is desorption of the molecules formed. Such a heterogeneous process of recombination of atoms on surfaces can be depicted schematically as follows:

$$A + S \rightleftarrows A(S)$$
$$A + A(S) \rightleftarrows A_2(S)$$
$$A_2(S) \rightleftarrows A_2 + S$$

A heterogeneous reaction of recombination of atoms is characterized by a quite definite activation energy. The latter is equal to 0.9 kcal/mol for the recombination of hydrogen atoms on the surface of glass, and to 3 kcal/mol on the surface of platinum. The higher value for platinum is explained by the greater strength of the bond between atomic hydrogen and platinum.

# CHAPTER 3

# FUNDAMENTALS OF MOLECULAR-KINETIC THEORY

The basic theoretical problem in chemical kinetics is to create such a system of views and equations that would make it possible to calculate the rate of a process on the basis of the molecular parameters of the reactants and the external conditions in which the process proceeds. The molecular parameters include the mass of the reacting molecules, their shape and size, the order of the bonds of separate atoms and atomic groups in a molecule, the energy characteristic of the individual bonds, and the complex of the possible energy states of a molecule. By external conditions are meant the pressure (or concentrations), temperature, and the conditions in which the process is conducted (for example, the conducting of a reaction in static conditions or in a flow system). An important stage in the solution of the problem is the application of the molecular-kinetic theory to the interpretation of kinetic laws in chemical transformations. For this reason the present chapter is devoted to the fundamentals of the molecular-kinetic theory that will be used later for solving the problem posed above.

**3.1. Boltzmann Distribution Law.** Let us consider an isolated system consisting of $N$ identical molecules having different energies and occupying a constant volume $V$. Let each of $N_1$ molecules have the energy $\varepsilon_1$, each of $N_2$ molecules the energy $\varepsilon_2$, etc., or, in other words, $N_1$ molecules are in the energy level $\varepsilon_1$, $N_2$ molecules in the energy level $\varepsilon_2$, etc. The total energy of the system will obviously be

$$E = N_1\varepsilon_1 + N_2\varepsilon_2 + N_3\varepsilon_3 + \ldots = \sum N_i\varepsilon_i \tag{3.1}$$

and the numbers $N$, $N_1$, $N_2$, etc. are related as follows:

$$N = N_1 + N_2 + N_3 + \ldots = \sum N_i \tag{3.2}$$

We shall consider the state of the system to be known and definite if the distribution of the molecules by energy levels is known, i.e. the numbers $N_1$, $N_2$, $N_3$, etc. are known.

The thermodynamic (statistical) probability (see Vol. 1, Sec. 3.8) of the given state of the system being considered is determined by

the equation

$$P = \frac{N!}{N_1!\,N_2!\,N_3!\ldots} = \frac{N!}{\prod_i N_i!} \tag{3.3}$$

where $\prod_i$ is the product of $i$ factors.

A definite relation is known to exist between the probability of the state of a system and its entropy, namely,

$$S = k \ln P + C \tag{3.4}$$

where $k$ = Boltzmann constant
$C$ = arbitrary constant.

Insertion of Eq. (3.3) into Eq. (3.4) gives

$$\ln P = \frac{S-C}{k} = \ln N! - \ln N_1! - \ln N_2! - \ln N_3! - \ldots =$$

$$= \ln N! - \sum \ln N_i! \tag{3.5}$$

Since in molecular systems the values of $N_i$ are very great, we can apply Stirling's approximation without any appreciable error:

$$\ln N! = N \ln N - N \tag{3.6}$$

Hence

$$\frac{S-C}{k} = N \ln N - N - \sum N_i \ln N_i + \sum N_i = N \ln N - \sum N_i \ln N_i \tag{3.7}$$

Equation (3.7), the same as Eqs. (3.3) and (3.4), is true for any state of a system. We shall use this equation to find the laws characterizing the states of equilibrium when $S$ and $P$ acquire their maximum values. Let us consider all the possible changes in the entropy due to changes in the numbers $N_i$, i.e.

$$dS_1 = \frac{dS}{dN_1}\,dN_1; \quad dS_2 = \frac{dS}{dN_2}\,dN_2;$$

$$dS_3 = \frac{dS}{dN_3}\,dN_3, \ldots$$

In a state of equilibrium the total change in the entropy of a system when the mass and energy are constant is equal to zero, i.e.

$$\delta S = \sum dS_i = 0 \tag{3.8}$$

Differentiation of Eq. (3.7) with respect to $N_i$ yields

$$dS_1 = -k\,(1 + \ln N_1)\,dN_1$$

similarly

$$dS_2 = -k\,(1 + \ln N_2)\,dN_2, \text{ etc.}$$

Summating all the increments of $S$ and taking into account that $k$ cannot be equal to zero, we get the condition for the maximum

of the entropy:

$$\sum (\ln N_i + 1)\, dN_i = 0 \tag{3.9}$$

This equation ensuing from the condition of equilibrium must be supplemented, for an isolated system, with two more conditions expressing the constancy of the total number of molecules and the total energy of the system, i.e.

$$\delta N = \sum dN_i = 0 \tag{3.10}$$

$$\delta E = \sum \varepsilon_i dN_i = 0 \tag{3.11}$$

Using the Lagrange method, we multiply Eqs. (3.10) and (3.11) respectively by indefinite factors $\lambda$ and $\mu$. Summation of the equations obtained and Eq. (3.9) yields

$$\sum (\ln N_i + 1 + \lambda + \mu\varepsilon_i)\, dN_i = 0 \tag{3.12}$$

It should further be noted that not all of the quantities $dN_i$ are independent ones, since they are related with one another by Eqs. (3.10) and (3.11), with the aid of which two differentials can be expressed through the remaining ones. The arbitrary factors $\lambda$ and $\mu$, however, can always be so selected that two coefficients of the differentials $dN_i$ in sum (3.12) are equal to zero, for example

$$\ln N_1 + 1 + \lambda + \mu\varepsilon_1 = 0$$

and

$$\ln N_2 + 1 + \lambda + \mu\varepsilon_2 = 0$$

There will now remain in sum (3.12) only addends containing independently changing quantities $dN_i$, and in the general case the sum can be equal to zero only when each of the remaining $i - 2$ coefficients is equal to zero. Thus, for an isolated system in a state of equilibrium the following equation holds:

$$\ln N_i + 1 + \lambda + \mu\varepsilon_i = 0 \tag{3.13}$$

which can also be written as follows

$$N_i = Ae^{-\mu\varepsilon_i} \tag{3.14}$$

where $A = e^{-(\lambda+1)}$

It can be shown that $\mu = 1/kT$ and Eq. (3.14) can be presented in the form of the basic equation of the Boltzmann law:

$$N_i = Ae^{-\varepsilon_i/kT} \tag{3.15}$$

according to which *in an equilibrium system the number of molecules having a certain energy* $\varepsilon$ *is proportional to the factor* $e^{-\varepsilon/kT}$. The latter is called the *Boltzmann factor*. The quantity $A$ in Eq. (3.15)

depends on the temperature, the number of molecules in the system, and also on the properties of the molecules themselves.

The Boltzmann law can be written in a different form:

$$\frac{N_i}{N} = \frac{e^{-\varepsilon_i/kT}}{\sum e^{-\varepsilon_i/kT}} = \frac{e^{-\varepsilon_i/kT}}{Q} \tag{3.16}$$

where $Q = \sum e^{-\varepsilon_i/kT}$ is the *partition function* (see Vol. 1, Sec. 10.1).

Since the distribution law was derived for a system having a constant volume, by dividing the numbers of molecules $N_i$ and $N$ by this volume, we get an expression for the concentrations:

$$\frac{n_i}{n} = \frac{e^{-\varepsilon_i/kT}}{Q} \tag{3.17}$$

where $n_i$ and $n$ are the number of molecules per cubic centimetre, i.e. the concentrations.

Let us consider a more complicated system, namely, one consisting of $N$ molecules of species A and $N'$ molecules of species B. Let the molecules of the first species be distributed among the energy levels $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i$, and those of the second species among the energy levels $\varepsilon'_1, \varepsilon'_2, \ldots, \varepsilon'_j$. If in a certain state the corresponding distribution numbers are equal to $N_1, N_2, \ldots, N_i$ and $N'_1, N'_2, \ldots, N'_j$, then the thermodynamic probability of such a state is determined by the equation

$$P = \frac{N!}{N_1!\,N_2!\ldots N_i!}\,\frac{N'!}{N'_1!\,N'_2!\ldots N'_j!}$$

Using as previously Stirling's approximation (3.6), we get

$$\ln P = N \ln N - \sum N_i \ln N_i + N' \ln N' - \sum N_j \ln N_j$$

Here the condition of the maximum probability will be

$$\sum (\ln N_i + 1)\, dN_i + \sum (\ln N_j + 1)\, dN_j = 0 \tag{3.18}$$

This condition should be supplemented with three additional ones, two of which express the constancy of the total number of molecules of each type, namely,

$$\sum_i dN_i = 0 \tag{3.19}$$

and

$$\sum_j dN_j = 0 \tag{3.20}$$

while the third one is connected with the constancy of the total energy

$$\sum \varepsilon_i dN_i + \sum \varepsilon_j\, dN_j = 0 \tag{3.21}$$

since we obviously cannot speak of the constancy of the store of energy in the complex of each species of molecules separately.

Multiplying Eqs. (3.19) and (3.20) by the arbitrary factors $\lambda$ and $\lambda'$, and Eq. (3.21) by the factor $\mu$, and summating the expressions obtained, we get

$$\sum (\ln N_i + 1 + \lambda + \mu\varepsilon_i)\, dN_i + \\ + \sum (\ln N_j + 1 + \lambda' + \mu\varepsilon_j) dN_j = 0 \qquad (3.22)$$

Since $dN_i$ and $dN_j$ are mutually independent, the general condition of equilibrium (3.22) is observed if all the coefficients of $dN_i$ and $dN_j$ are equal to zero, i.e.

$$\left.\begin{aligned} &\ln N_i + 1 + \lambda + \mu\varepsilon_i = 0 \\ \text{and} \quad & \\ &\ln N_j + 1 + \lambda' + \mu\varepsilon_j = 0 \end{aligned}\right\} \qquad (3.23)$$

Thus, for a mixture of gases we get two equations similar to Eq. (3.14):

$$\left.\begin{aligned} &N_i = Ae^{-\mu\varepsilon_i} \\ \text{and} \quad & \\ &N_j = A'e^{-\mu\varepsilon_j} \end{aligned}\right\} \qquad (3.24)$$

A glance at these equations shows that the factor $A$ indeed depends on the nature of the gas, while the quantity $\mu$ remains constant in all cases and, as can be shown, equals $1/kT$. Consequently, for a mixture of two gases two distribution laws are true, namely,

$$\left.\begin{aligned} &N_i = Ae^{-\varepsilon_i/kT} \\ \text{and} \quad & \\ &N_j = A'e^{-\varepsilon_j/kT} \end{aligned}\right\} \qquad (3.25)$$

The relations obtained can be applied to a mixture of gases with any number of components.

**3.2. Maxwell-Boltzmann Law.** In deriving the Boltzmann exponential law in the form of Eqs. (3.15), (3.25) or (3.16) no account was taken of the position of the molecules in space and no mention was made of the nature of the energy $\varepsilon$ which a molecule may have. For this reason the equations obtained can be used to characterize the distribution of the total energy and any kind of energy, whether it is translational, rotational or vibrational energy, etc., on condition, however, that the total energy of the system being considered is constant. Further, no account was taken of the possibility of a molecule being in intermediate energy levels (between $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i$). On the other hand, no mention was made of the mutual arrangement of levels $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i$, therefore, considering that they are arranged infinitely close to one another, we can assume that the distribution found is continuous. In this section we consider the application of the Boltzmann law to systems in which the energy

of the molecules changes continuously from zero to an infinitely great value.

Let us solve the problem as to what number of molecules having an energy between $\varepsilon$ and $\varepsilon + d\varepsilon$ can simultaneously be characterized by values of the impulses within the ranges from $p_1$ to $(p_1 + dp_1)$, from $p_2$ to $(p_2 + dp_2)$, etc. and are in the part of space with coordinates ranging from $q_1$ to $(q_1 + dq_1)$, from $q_2$ to $(q_2 + dq_2)$, etc. In the general form the energy of a molecule as the sum of the kinetic and potential energies can be represented as a function of coordinates and impulses:

$$\varepsilon = \varepsilon_p + \varepsilon_k = w(q_1, q_2, q_3, \ldots, q_s) + \frac{1}{2m}(p_1^2 + p_2^2 + p_3^2 + \ldots + p_s^2) \tag{3.26}$$

It is considered here that to describe the position of a molecule and all its moving parts in a phase space we must have $s$ space coordinates ($q$) and $s$ impulses ($p$) characterizing the kinetic energies of all possible motions of the molecules connected with a change in the coordinates $q$. The number of molecules ($dN$) satisfying the characteristic given above is proportional to an element of a multidimensional volume

$$dq_1 dq_2 dq_3 \ \ldots \ dq_s dp_1 dp_2 dp_3 \ \ldots \ dp_s$$

in exactly the same way as the number of molecules in an element of volume of three-dimensional space is proportional to the volume of this element. The number $dN$ should obviously be proportional to the Boltzmann factor $Ae^{-\varepsilon/kT}$ and the total number of molecules $N$ in the system.

Thus, introducing a new proportionality factor $C$, we get

$$dN = CNe^{-\varepsilon/kT} dq_1, dq_2, \ldots, dq_s, dp_1, dp_2, \ldots, dp_s \tag{3.27}$$

Let us apply Eq. (3.27) to an ideal monatomic gas in which the state of each molecule is completely characterized by three space coordinates and three corresponding impulses. The results obtained will also relate to an ideal gas with molecules of any complicacy, if we consider that these molecules are elastic spheres and take into account only the energy of translational motion. Since $s$ in the given case is equal to three, we can write

$$dN = CNe^{-\varepsilon/kT} dx\, dy\, dz\, m\,d\dot{x}\, m\,d\dot{y}\, m\,d\dot{z} \tag{3.28}$$

where $\dot{x}$, $\dot{y}$ and $\dot{z}$ are components of the velocity of a molecule.

The total number of molecules $N$ can obviously be found by integration of Eq. (3.28). The limit of integration with respect to the space coordinates $x$, $y$ and $z$ is restricted by the volume of the system, and the limit of integration with respect to velocities—by the total

energy of the system:

$$\int_0^N dN = CN \int\int_{-\infty}^{+\infty} \int\int\int e^{-\varepsilon/kT} dx\, dy\, dz\, m\, d\dot{x}\, m\, d\dot{y}\, m\, d\dot{z} \qquad (3.29)$$

Since $\int_0^N dN = N$, we can cancel $N$. The integral $\int\int\int dx\, dy\, dz$ is equal to the total volume of the system $V$. Hence

$$1 = CVm^3 \int \int_{-\infty}^{+\infty} \int e^{-\varepsilon/kT} d\dot{x}\, d\dot{y}\, d\dot{z} \qquad (3.30)$$

For an ideal monatomic gas the energy of a molecule will be

$$\varepsilon = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \qquad (3.31)$$

and since the velocities $\dot{x}$, $\dot{y}$ and $\dot{z}$ are mutually independent, integration can be so carried out separately with respect to three variables that

$$\frac{1}{C} = Vm^3 \int_{-\infty}^{+\infty} e^{-m\dot{x}^2/2kT} d\dot{x} \int_{-\infty}^{+\infty} e^{-m\dot{y}^2/2kT} d\dot{y} \int_{-\infty}^{+\infty} e^{-m\dot{z}^2/2kT} d\dot{z} \qquad (3.32)$$

and consists in finding three integrals of one type.

It is known that $\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$. Consequently

$$\frac{1}{C} = Vm^3 \left(\frac{2\pi kT}{m}\right)^{3/2} = (2\pi mkT)^{3/2} V \qquad (3.33)$$

The value of the constant $C$ has been obtained for molecules moving in three-dimensional space, i.e. having three degrees of freedom of translational motion. If the motion is limited to a plane with the dimensions $l_1 \times l_2$, it can easily be shown by a similar transformation of Eq. (3.29) that the respective constant will have the value

$$\frac{1}{C'} = (2\pi mkT)\, l_1 l_2 \qquad (3.34)$$

In one-dimensional motion along the distance $l$ we get

$$\frac{1}{C''} = (2\pi mkT)^{1/2}\, l \qquad (3.35)$$

Integration of the left-hand part of Eq. (3.27) with respect to the total number of molecules, and of the right-hand part with respect

to all possible values of the coordinates and impulses yields

$$N = NC \int \ldots \int e^{-\varepsilon/kT} dq_1 \ldots dq_s dp_1 \ldots dp_s \tag{3.36}$$

whence

$$1/C = \int \ldots \int e^{-\varepsilon/kT} dq_1 \ldots dq_s dp_1 \ldots dp_s \tag{3.37}$$

Comparing Eqs. (3.37) and (3.27), we have

$$\frac{dN}{N} = \frac{e^{-\varepsilon/kT} dq_1 \ldots dq_s dp_1 \ldots dp_s}{\int \ldots \int e^{-\varepsilon/kT} dq_1 \ldots dq_s dp_1 \ldots dp_s} \tag{3.38}$$

The distribution law written in the form of Eq. (3.38) is called the *Maxwell-Boltzmann* law and is one of the main laws of statistical physics. We can use it to solve many problems of physical chemistry. J. Maxwell himself used this law for finding the distribution of molecules by velocities (the Maxwell law), and L. Boltzmann for finding the distribution of molecules by energies. The significance of the Maxwell-Boltzmann law also consists in the possibility of calculating different mean statistical properties of molecules—velocities, energies, etc.

The mean value $\bar{P}$ of a property $P$ depending on the coordinates and impulses of the molecules can be determined by multiplying the number of molecules in a given group by the value of the property $P$ constant for the molecules of the given group, by summation of all the possible products of this type and dividing the sum obtained by the total number of molecules, i.e.

$$\bar{P} = \frac{\int P\,dN}{N} = C \int \ldots \int e^{-\varepsilon/kT} P\, dq_1 \ldots dq_s dp_1 \ldots dp_s =$$

$$= \frac{\int \ldots \int e^{-\varepsilon/kT} P\, dq_1 \ldots dq_s dp_1 \ldots dp_s}{\int \ldots \int e^{-\varepsilon/kT} dq_1 \ldots dq_s dp_1 \ldots dp_s} \tag{3.39}$$

This equation is used to compute the mean statistical values of different properties (for examples see the following section). Our calculations will relate to an ideal monatomic gas for which Eq. (3.39) can be written in the form

$$\bar{P} = \frac{\int\int\int\int\int\int e^{-\varepsilon/kT} P\, dx\, dy\, dz\, dp_u\, dp_v\, dp_w}{\int\int\int\int\int\int e^{-\varepsilon/kT} dx\, dy\, dz\, dp_u\, dp_v\, dp_w} \tag{3.40}$$

The values of the integral in the denominator already known from Eqs. (3.33), (3.34) and (3.35) will also be used in the calculations.

**3.3. Application of Maxwell-Boltzmann Law to an Ideal Gas.** The following examples illustrate application of the Maxwell-Boltzmann law to an ideal gas.

1. *Determining the Mean Value of the Component of the Velocity of a Molecule in a Given Direction.* Let us compute the mean value of the velocity $u$ along one of the axes of coordinates, for example $x$, assuming that $x$ can have only positive values, and all the possible velocities are within the limits from 0 to $\infty$. This assumption is explained by the circumstance that we are interested only in the mean absolute value of the velocity along the $x$-axis. This mean value is the same for motion from the right to the left and from the left to the right. Since in the present case we are not interested in any other components of the total velocity of a molecule or in a change in the position of the molecule relative to the axes $y$ and $z$, we must take into account the only variable impulse $mu$ and the change in only one space coordinate $x$. Consequently, in accordance with Eq. (3.40), we get

$$\bar{u} = \frac{\int\limits_0^{\infty} \int e^{-mu^2/2kT} u\, dx\, m\, du}{\int\limits_{-\infty}^{+\infty} \int e^{-mu^2/2kT} dx\, m\, du} \tag{3.41}$$

The integral in the denominator [see Eq. (3.35)] is equal to $(2\pi\, mkT)^{1/2} l$, where $l$ is the value of the coordinate $x$ that can be reached in motion in the given direction. In the numerator integration from 0 to $\infty$ with respect to all the values of $x$ gives $l$, and the integral

$$m \int\limits_0^{\infty} e^{-mu^2/2kT} u\, du$$

is easily taken by substitution of $y = mu^2/2kT$ and is equal to $kT$. Thus the numerator is equal to $l\, kT$, and the mean velocity sought is

$$\bar{u} = \left(\frac{kT}{2\pi m}\right)^{1/2} \tag{3.42}$$

This expression for the mean velocity of motion in a given direction is used in the theory of chemical kinetics (the theory of the activated complex).

2. *Determining the Mean Value of the Square of the Velocity of One-Dimensional Motion and the Mean Kinetic Energy of a Molecule for One Degree of Freedom.* Again taking into account the single variable impulse $mu$ and one coordinate $x$, we get

$$\overline{u^2} = \frac{\int \int\limits_{-\infty}^{+\infty} e^{-mu^2/2kT} u^2\, dx\, m\, du}{\int \int\limits_{-\infty}^{+\infty} e^{-mu^2/2kT} dx\, m\, du} \tag{3.43}$$

It should be noted that in the numerator of this expression we integrate with respect to the impulse from $-\infty$ to $+\infty$, i.e. with respect to all possible values of the velocity, both positive and negative ones. This is due to the fact that the value of the square of the velocity does not depend on its direction. The integral in the denominator is equal to $(2\pi\, mkT)^{1/2}l$. In the numerator integration with respect to the coordinate $x$ gives the value $l$. There thus remains the integral

$$m \int_{-\infty}^{+\infty} e^{-mu^2/2kT} u^2\, du$$

Let us denote $m/2kT$ by $a$. Integration will thus be reduced to taking a tabulated integral of the form $m \int_{-\infty}^{+\infty} e^{-ax^2} x^2 dx$, which is equal to

$$\frac{1}{2} m \left(\frac{\pi}{a^3}\right)^{1/2} = \left(\frac{2\pi}{m}\right)^{1/2} (kT)^{3/2}$$

Consequently

$$\overline{u^2} = \frac{\left(\frac{2\pi}{m}\right)^{1/2} (kT)^{3/2}\, l}{(2\pi mkT)^{1/2}\, l} = \frac{kT}{m} \tag{3.44}$$

and the mean kinetic energy of a molecule for one degree of freedom

$$\frac{1}{2} m\overline{u^2} = \frac{1}{2} kT \tag{3.45}$$

3. *Determining the Mean Velocity of Molecules in Three-Dimensional Space.* The total kinetic energy of a molecule $\varepsilon$ can be expressed both in terms of the total velocity $c$, and of its components along the coordinate axes $u$, $v$ and $w$:

$$\varepsilon = \frac{1}{2} mc^2 = \frac{1}{2} m (u^2 + v^2 + w^2) \tag{3.46}$$

According to Eq. (3.39), the mean value of the velocity $\bar{c}$ (if we omit integration with respect to the space coordinates, which, as should be clear from the previous material, gives the volume of the system as a factor in both the numerator and the denominator), will be

$$\bar{c} = \frac{\int \int_{-\infty}^{+\infty} \int e^{-\varepsilon/kT} c\, dp_u\, dp_v\, dp_w}{\int \int_{-\infty}^{+\infty} \int e^{-\varepsilon/kT}\, dp_u\, dp_v\, dp_w} \tag{3.47}$$

The integral in the denominator of Eq. (3.47) is equal to $(2\pi mkT)^{3/2}$ [see Eq. (3.33)]. Consequently

$$\bar{c} = \left(\frac{m}{2\pi kT}\right)^{3/2} \int \int_{-\infty}^{+\infty} \int e^{-mc^2/2kT} c \, du \, dv \, dw \tag{3.48}$$

For further integration it is necessary to transfer from rectangular coordinates to spherical ones, introducing a radius-vector that is identical in the given case to the modulus of the vector of the velocity $c$, and also the longitude $\varphi$ and latitude $\nu$. The product $du\,dv\,dw$ can be considered as an element of volume. In spherical coordinates this volume can be expressed through the radius-vector, the latitude and longitude, namely,

$$du\,dv\,dw = c^2 \sin \nu \, d\nu \, d\varphi \, dc \tag{3.49}$$

Eq. (3.48) will therefore become

$$\bar{c} = \left(\frac{m}{2\pi kT}\right)^{3/2} \int\int\int e^{-mc^2/2kT} c^3 \sin \nu \, d\nu \, d\varphi \, dc \tag{3.50}$$

and the limits of integration (for taking into account all possible values of the velocity) should be as follows: with respect to the velocity from 0 to $\infty$, to the latitude from 0 to $\pi$ and the longitude from 0 to $2\pi$. Since the variables $\nu$, $\varphi$ and $c$ are independent, the triple integral can be replaced by three integrals:

$$\bar{c} = \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^{2\pi} d\varphi \int_0^{\pi} \sin \nu \, d\nu \int_0^{\infty} e^{-mc^2/2kT} c^3 \, dc \tag{3.51}$$

The first two integrals will obviously give the factor $4\pi$, and the third integral is easily reduced to a tabulated one and is equal to $2\,(kT/m)^2$. We thus finally obtain

$$\bar{c} = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \times 2 \left(\frac{kT}{m}\right)^2 = \left(\frac{8kT}{\pi m}\right)^{1/2} \tag{3.52}$$

4. *Determining the Mean Square Value of the Velocity for Three Degrees of Freedom, the Mean Value of the Total Kinetic Energy of a Molecule and the Root-Mean-Square Velocity.* Repeating the reasoning of subsection "3", but inserting $c^2$ instead of $c$ in the initial equation [of type (3.47)], we get

$$\overline{c^2} = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \int_0^{\infty} e^{-mc^2/2kT} c^2 \, dc \tag{3.53}$$

The integral in Eq. (3.53) is equal to $3\,(\pi/2)^{1/2}\,(kT/m)^{5/2}$. Consequently

$$\overline{c^2} = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \times 3 \left(\frac{\pi}{2}\right)^{1/2} \left(\frac{kT}{m}\right)^{5/2} = \frac{3kT}{m} \tag{3.54}$$

The mean value of the total kinetic energy of a molecule can be written as follows on the basis of Eq. (3.54):

$$\frac{1}{2} m\bar{c}^2 = \frac{3}{2} kT \tag{3.55}$$

It is obviously three times greater than the mean energy calculated for one degree of freedom [Eq. (3.45)].

Finally, the root-mean-square velocity is determined as the square root of the mean square of the velocity

$$\sqrt{\bar{c}^2} = \left(\frac{3kT}{m}\right)^{1/2} \tag{3.56}$$

The latter quantity obviously differs from the mean velocity determined by Eq. (3.52), namely

$$\sqrt{\bar{c}^2}/\bar{c} = (3\pi/8)^{1/2} = 1.085$$

5. *Determining the Distribution of the Molecules by Velocities (the Maxwell Law)*. Let us first find the number of molecules $dN_u$ whose component velocity $u$ along the $x$-axis is within the limits from $u$ to $u + du$, regardless of the values of the other velocity components, and also of the position of the molecules in space. On the basis of the general law of distribution in the form most convenient for the given case [see Eq. (3.38)], it is possible to omit integration with respect to the space coordinate. Also, account should be taken of the change in only one impulse $p_u$, since the values of the two other impulses make no difference to us. With account of these assumptions, Eq. (3.38) can be written as follows:

$$\frac{dN_u}{N} = \frac{e^{-\varepsilon_u/kT}\, dp_u}{\int_{-\infty}^{+\infty} e^{-\varepsilon_u/kT}\, dp_u} \tag{3.57}$$

This equation expresses the fraction of molecules whose impulse $p_u$ is within the limits from $p_u$ to $p_u + dp_u$, and whose velocity component $u$ is obviously within the limits from $u$ to $u + du$. Since the integral in the denominator [see Eq. (3.35)] is equal to $(2\pi mkT)^{1/2}$, we finally get the expression

$$\frac{dN_u}{N} = \frac{e^{-mu^2/2kT} m\, du}{(2\pi mkT)^{1/2}} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mu^2/2kT}\, du \tag{3.58}$$

which is the Maxwell law of distribution of molecules by velocities for one degree of freedom. It is quite clear that equations absolutely similar to Eq. (3.58) can be written for the other velocity components, i.e. $v$ and $w$.

Let us now solve a more complicated problem, i.e. determine the number of molecules $dN_c$ whose total velocity ranges from $c$ to

$c + dc$. For this purpose let us rewrite distribution law (3.38), omitting, as previously, integration with respect to the space coordinates (since the position of the molecules in space is of no difference to us), but now taking into account the change in three impulses

$$\frac{dN'}{N} = \frac{e^{-\varepsilon_c/kT}\, dp_u\, dp_v\, dp_w}{\int\int\int_{-\infty}^{+\infty} e^{-\varepsilon_c/kT}\, dp_u\, dp_v dp_w} \tag{3.59}$$

where $dN'$ = number of molecules whose impulse components have values within the limits from $p_u$ to $p_u + dp_u$, from $p_v$ to $p_v + dp_v$ and from $p_w$ to $p_w + dp_w$

$\varepsilon_c$ = total kinetic energy of a molecule equal to $mc^2/2$.

Passing over from impulses to velocities and taking into account the value of the integral in the denominator, equal to $(2\pi\, mkT)^{3/2}$, let us rewrite Eq. (3.59) in the form

$$\frac{dN'}{N} = \frac{m^3 e^{-\varepsilon_c/kT}\, du\, dv\, dw}{(2\pi mkT)^{3/2}} \tag{3.60}$$

or, with account of Eq. (3.49)

$$\frac{dN'}{N} = \frac{m^3 e^{-\varepsilon_c/kT} c^2 \sin\nu\, d\nu\, d\varphi\, dc}{(2\pi mkT)^{3/2}} \tag{3.61}$$

Now $dN'$ can be interpreted as the number of molecules with total velocities that range from $c$ to $c + dc$, and in direction are confined within the limits of the following spherical coordinates: latitude from $\nu$ to $\nu + d\nu$ and longitude from $\varphi$ to $\varphi + d\varphi$. Since we are interested in the number of molecules $dN_c$ having velocities from $c$ to $c + dc$ regardless of the direction of their motion, Eq. (3.61) should be integrated with respect to all possible directions, as was already done in deducing formula (3.52), i.e. with respect to latitude from 0 to $\pi$ and to longitude from 0 to $2\pi$. As already shown, integration gives the factor $4\pi$. Consequently,

$$\frac{dN_c}{N} = \frac{m^3 4\pi e^{-\varepsilon_c/kT} c^2\, dc}{(2\pi mkT)^{3/2}} = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{m}{kT}\right)^{3/2} e^{-mc^2/2kT} c^2\, dc \tag{3.62}$$

Equation (3.62) expresses the Maxwell law for the distribution of molecules by total velocities. It will be convenient to consider it in greater detail with the aid of the chart shown in Fig. 3.1, in which the content in per cent of molecules with velocities from $c$ to $c + dc$ is laid off along the $y$-axis, i.e. $y = \frac{1}{N}\frac{dN_c}{dc} 100$, and the velocity $c$ is laid off along the $x$-axis. A glance at the figure shows that the distribution curve has a maximum whose ordinate and abscissa

depend on the temperature. The velocity corresponding to the maximum of the curve is called the *most probable velocity* ($\alpha$), since the greatest number of molecules ($y$) travels with this velocity. It is easy to find the value of $\alpha$ by differentiation of $y$ with respect to $c$ and equating the first derivative to zero, i.e.

$$\alpha = c_{max} = \left(\frac{2kT}{m}\right)^{1/2} \quad (3.63)$$

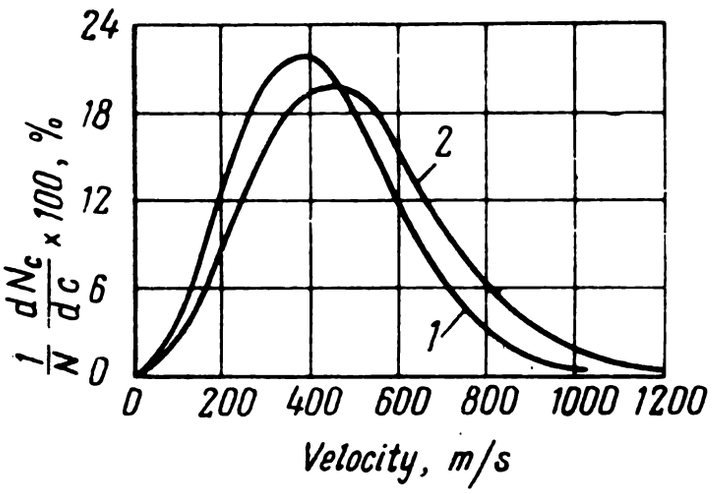


Fig. 3.1. Distribution of oxygen molecules by velocities:
1—at $T = 273$ K; 2—at $T = 373$ K

We can see from a comparison of Eqs. (3.63), (3.52) and (3.56) that the most probable velocity differs both from the mean arithmetical and the root-mean-square values.

6. *Determining the Distribution of Molecules by Energies When the Energy is Expressed by the Sum of Two Quadratic Terms.* The form of the equation expressing the law of distribution of molecules by energies depends on the components forming the total energy of the molecules. For example, the total kinetic energy of a molecule can be represented by the sum of three addends:

$$\varepsilon_c = \frac{1}{2}mc^2 = \frac{1}{2}mu^2 + \frac{1}{2}mv^2 + \frac{1}{2}mw^2$$

where $u$, $v$ and $w$ = components of the total velocity $c$ of a molecule, as previously
$m$ = mass of a molecule.

In this case the energy is said to be expressed by the sum of three quadratic terms. If in addition to translational motion other forms of motion must be taken into account, for example the vibrations of atoms in a molecule, additional terms will appear in the expression for the energy. For example, the energy of harmonic vibration is expressed by two quadratic terms, namely, for the potential energy $\frac{1}{2}fq^2$ (here $q$ shows a change in the coordinate, and $f$ is a factor of proportionality—a force constant), and for the kinetic energy $\frac{1}{2m}p^2$. Consequently, if for a complex molecule at sufficiently high temperatures it is necessary to take into account $n$ different kinds of vibrations of atoms, then $2n$ quadratic terms will correspondingly appear in the expression for the energy.

The simplest and practically most important form of the law of distribution of molecules by energies is obtained when the energy

is expressed by the sum of two quadratic terms. It is the most convenient to consider the case when all the energy is kinetic, i.e.

$$\varepsilon = \frac{1}{2} mc^2 = \frac{1}{2} m (u^2 + v^2)$$

which corresponds to the motion of molecules in a plane, for example in an adsorption layer. It can be shown, however, that the form of the distribution law does not depend on the kind of energy, since it is only important to know how many quadratic terms it can be expressed by. For this reason on the same grounds we can relate the equation being considered to the distribution of molecules by energies of one form of vibrational motion, say in diatomic molecules.

Since we are not interested in the position of the molecules in space, we can write the general law of distribution (3.38) as follows:

$$\frac{dN'}{N} = \frac{e^{-\varepsilon/kT}\, dp_u\, dp_v}{\iint\limits_{-\infty}^{+\infty} e^{-\varepsilon/kT}\, dp_u\, dp_v} \tag{3.64}$$

where $dN'$ is the number of molecules whose impulses regardless of their position in space have values from $p_u$ to $p_u + dp_u$ and from $p_v$ to $p_v + dp_v$.

Inserting the value of the integral in the denominator from Eq. (3.34), we get

$$\frac{dN'}{N} = \frac{m^2 e^{-\varepsilon/kT}\, du\, dv}{2\pi mkT} \tag{3.65}$$

Passing over from rectangular coordinates to polar ones, we see that the element of area $du\, dv$ on the plane of velocities can be replaced by the product of an element of a circle $c\, d\theta$ and the increment of the radius-vector $dc$. (Here $\theta$ is the angle travelled by the radius-vector.) Hence

$$du\, dv = c\, d\theta\, dc \tag{3.66}$$

Since we are interested in the energy of the molecules, and not in the directed velocity, Eq. (3.66) should obviously be integrated from 0 to $2\pi$. This gives directly $dudv = 2\pi cdc$, and since $\varepsilon = \frac{1}{2} mc^2$ and $d\varepsilon = mcdc$, instead of Eq. (3.65) we get

$$\frac{dN''}{N} = \frac{1}{kT} e^{-\varepsilon/kT}\, d\varepsilon \tag{3.67}$$

where $dN''$ is the number of molecules whose energy is within the limits from $\varepsilon$ to $\varepsilon + d\varepsilon$.

The fraction $dN''/N$ characterizes the portion of the molecules having an energy within the limits indicated above.

To solve a number of problems of physical chemistry, it is important to know the number of molecules $N_{\varepsilon_0}$ having an energy equal

to or greater than a certain definite value $\varepsilon_0$. To find this number of molecules we must integrate Eq. (3.67) from $\varepsilon_0$ to $\infty$:

$$\frac{N_{\varepsilon_0}}{N} = \frac{1}{kT} \int_{\varepsilon_0}^{\infty} e^{-\varepsilon/kT} d\varepsilon = e^{-\varepsilon_0/kT}$$

or

$$N_{\varepsilon_0} = Ne^{-\varepsilon_0/kT} \tag{3.68}$$

It should be noted that Eq. (3.68) is the only one in which the number of molecules is proportional to the Boltzmann factor without a coefficient of proportionality depending on the temperature. It shows the number of molecules from among the total number $N$ that have an energy equal to or greater than $\varepsilon_0$ if the energy is expressed by two quadratic terms.

7. *Determining the Distribution of Molecules by Energies When the Energy is Expressed by the Sum of 2s Quadratic Terms.* It was noted in subsection 6 that if the energy of molecules is expressed by the sum of a certain number of terms which are quadratic relative either to the space coordinates ($q_i$) or to the impulses ($p_i$), the form of the distribution law does not depend on how many terms there are in the expression for the kinetic energy and how many in the one for the potential energy. The derivation of the law is simplified, however, if we consider the same number of terms $s$ expressing the potential $\left(\frac{1}{2} fq^2\right)$ and the kinetic $\left(\frac{1}{2m} p^2\right)$ energy. From the physical viewpoint, this corresponds to the assumption that the summary motion of the molecules is represented by $s$ independent harmonic vibrators. In this case the energy of a molecule can be written as

$$\varepsilon = \frac{1}{2} f_1 q_1^2 + \frac{1}{2} f_2 q_2^2 + \ldots + \frac{1}{2} f_s q_s^2 + \frac{1}{2m} p_1^2 + \frac{1}{2m} p_2^2 + \ldots +$$

$$+ \frac{1}{2m} p_s^2 = \frac{1}{2} \sum^{s} f_i q_i^2 + \frac{1}{2} \sum^{s} \left(\frac{p_i^2}{m}\right) \tag{3.69}$$

The frequency of vibrations of a harmonic vibrator is related to the mass of a vibrating particle and the force constant $f$ as follows

$$\nu_i = \frac{1}{2\pi} \left(\frac{f_i}{m_i}\right)^{1/2} \tag{3.70}$$

Inserting the value of $f_i$ from Eq. (3.70) into Eq. (3.69), we get

$$\varepsilon = \frac{1}{2} \sum^{s} (2\pi\nu_i)^2 m_i q_i^2 + \frac{1}{2} \sum^{s} (p_i^2/m) \tag{3.71}$$

Let us now apply the distribution law, writing it in the form of Eq. (3.38)

$$\frac{dN}{N} = \frac{e^{-\varepsilon/kT} dq_1 \ldots dq_s dp_1 \ldots dp_s}{\int \ldots \int e^{-\varepsilon/kT} dq_1 \ldots dq_s dp_1 \ldots dp_s.}$$

We shall find the values of the numerator and denominator in Eq. (3.71) by introducing the symbols

$$w_i = (2m_i)^{1/2} \pi \nu_i q_i \quad \text{and} \quad z_i = (2m_i)^{-1/2} p_i \tag{3.72}$$

We get

$$\varepsilon = \sum^{s} w_i^2 + \sum^{s} z_i^2 \tag{3.73}$$

Let us also assume that

$$\varepsilon = R^2 = \sum^{s} w_i^2 + \sum^{s} z_i^2 \tag{3.74}$$

and consider $R$ as the radius of a certain hypersphere of $2s$ dimensions whose components are the values of the variables $w_i$ and $z_i$.[1] The volume of such a hypersphere is

$$V = \frac{\pi^s R^{2s}}{s!} = \frac{\pi^s \varepsilon^s}{s!} \tag{3.75}$$

and we shall find an element of the volume by differentiation of Eq. (3.75):

$$dV = \frac{\pi^s}{(s-1)!} \varepsilon^{s-1} d\varepsilon \tag{3.76}$$

On the other hand, an element of volume of a hypersphere can be expressed as the product of the increments of the coordinates $w_i$ and $z_i$, i.e.

$$dV = dw_i \ldots dw_s dz_i \ldots dz_s$$

Let us now relate this product to our initial coordinates $q_i$ and $p_i$, for which purpose we differentiate Eq. (3.72). We get

$$dw_i = (2m_i)^{1/2} \pi \nu_i \, dq_i$$

and

$$dz_i = (2m_i)^{-1/2} dp_i$$

or

$$dq_i \, dp_i = (1/\pi \nu_i) \, dw_i \, dz_i$$

The product for all $2s$ coordinates can obviously now be written in the following form

$$dq_1 \ldots dq_s dp_1 \ldots dp_s = \left[\prod^{s}\left(\frac{1}{\pi \nu_i}\right)\right] dw_i \ldots dw_s dz_1 \ldots dz_s =$$

$$= \left[\prod^{s}\left(\frac{1}{\pi \nu_i}\right)\right] dV = \frac{\left[\prod^{s}\left(\frac{1}{\nu_i}\right)\right]}{(s-1)!} \varepsilon^{s-1} d\varepsilon \tag{3.77}$$

[1] Similar to the radius of a three-dimensional sphere, which is determined by the values of three coordinates: $R^2 = x^2 + y^2 + z^2$.

Using Eq. (3.77), let us find an expression for the numerator in the equation of the distribution law (3.38). We get

$$e^{-\varepsilon/kT}\,dq_1\ldots dq_s\,dp_1\ldots dp_s=\frac{\prod^{s}\left(\frac{1}{\nu_i}\right)}{(s-1)!}\,e^{-\varepsilon/kT}\varepsilon^{s-1}\,d\varepsilon \qquad (3.78)$$

We find the denominator in Eq. (3.38) by single integration of Eq. (3.78) with respect to all possible values of the energy from 0 to $\infty$, i.e.

$$\frac{\left[\prod^{s}\left(\frac{1}{\nu_i}\right)\right]}{(s-1)!}\int_0^{\infty} e^{-\varepsilon/kT}\varepsilon^{s-1}\,d\varepsilon=\left[\prod^{s}\left(\frac{1}{\nu_i}\right)\right](kT)^s$$

Thus, the final form of the distribution law will be

$$\frac{dN}{N}=\frac{e^{-\varepsilon/kT}\varepsilon^{s-1}\,d\varepsilon}{(kT)^s\,(s-1)!} \qquad (3.79)$$

where $dN$ is the number of molecules whose energy, expressed by $2s$ quadratic terms, is within the limits from $\varepsilon$ to $\varepsilon+d\varepsilon$.

Let us now find the number of molecules $N_{\varepsilon_0}$ with an energy equal to or greater than a value $\varepsilon_0$. For this purpose it is obviously necessary to integrate Eq. (3.79) from $\varepsilon_0$ to $\infty$, i.e.

$$\frac{N_{\varepsilon_0}}{N}=\frac{1}{(kT)^s\,(s-1)!}\int_{\varepsilon_0}^{\infty} e^{-\varepsilon/kT}\,\varepsilon^{s-1}d\varepsilon=$$

$$=e^{-\varepsilon_0/kT}\left[\frac{\left(\frac{\varepsilon_0}{kT}\right)^{s-1}}{(s-1)!}+\frac{\left(\frac{\varepsilon_0}{kT}\right)^{s-2}}{(s-2)!}+\ldots+1\right] \qquad (3.80)$$

This is an accurate expression for the sought fraction of molecules. In chemical kinetics, however, use is often made of an approximate formula that is obtained if in Eq. (3.80) we neglect all the terms in the series in brackets except the first one:

$$N_{\varepsilon_0}=N\frac{\left(\frac{\varepsilon_0}{kT}\right)^{s-1}}{(s-1)!}\,e^{-\varepsilon_0/kT} \qquad (3.81)$$

The approximate equation may be used only when the ratio $\varepsilon_0/kT$ is sufficiently great and the first term of the series is much greater than the remaining ones. It can easily be seen that when $s=1$, i.e. when there are two quadratic terms, Eq. (3.81) acquires the form of Eq. (3.68) obtained previously, i.e.

$$N_{\varepsilon_0}=Ne^{-\varepsilon_0/kT}$$

8. *Determining the Frequency of Collisions of Molecules against a Wall.* Let us determine the number of molecules $Z$ colliding with a flat surface having an area of one square centimetre during one second. Let us imagine an elementary area of this size selected on plane $yz$. If the mean velocity of the molecules along the $x$-axis is $\bar{u}$, it is quite clear that during one second all the molecules within a parallelepiped with the altitude $u$ will collide with the area under consideration. When the concentration of the molecules is $n$ cm$^{-3}$, the number of molecules within the volume of the parallelepiped is $n\bar{u}$. Thus the frequency of the collisions of the molecules against the wall is also equal to $n\bar{u}$, i.e.

$$Z = n\bar{u} \tag{3.82}$$

The mean velocity of the molecules in a given direction was calculated at the beginning of the present section [Eq. (3.42)].

Inserting this equation into Eq. (3.82), we get

$$Z = n\left(\frac{kT}{2\pi m}\right)^{1/2} \tag{3.83}$$

If, finally, we use the equation of state of an ideal gas $p = nkT$, the number of collisions of molecules with a flat surface having an area of 1 cm$^2$ during 1 s can also be written as follows:

$$Z = \frac{p}{(2\pi mkT)^{1/2}} \tag{3.84}$$

This equation, derived by Hertz in 1882, is used in studying processes of vaporization, condensation, adsorption, in heterogeneous chemical reactions, etc.

9. *Determining the Frequency of Double Collisions of Molecules.* In studying the rates of chemical reactions it is important to know the number of collisions occurring between two molecules of a gas in a unit of volume in a unit of time, i.e. the frequency of double collisions. Here both the total number of collisions and their number occurring with the observance of a limiting condition, most frequently an energy one, may be of interest. Let us first find the total number of double collisions.

The kinetic energy $\varepsilon$ of two molecules with the masses $m_1$ and $m_2$ can be expressed both through their total absolute velocities $c_1$ and $c_2$ in space and through the components of these velocities along three coordinate axes, i.e.

$$\varepsilon = \frac{1}{2}(m_1c_1^2 + m_2c_2^2) = \frac{1}{2}m_1(u_1^2 + v_1^2 + w_1^2) + \\ + \frac{1}{2}m_2(u_2^2 + v_2^2 + w_2^2) \tag{3.85}$$

It is more convenient, however, to consider not the motion of each of the two molecules separately, but the motion of their common centre of mass and the relative mutual motion of the molecules. Let us denote by $c$ the velocity of the common centre of mass. We shall find the components of this velocity, related by the expression

$$c^2 = u^2 + v^2 + w^2 \tag{3.86}$$

with a view to the circumstance that the component of the momentum (impulse) of the centre of mass $(m_1 + m_2)$ should be equal to the sum of the components of the momenta of the masses taken separately, i.e.

$$u\,(m_1 + m_2) = u_1 m_1 + u_2 m_2$$

or

$$u = \frac{u_1 m_1 + u_2 m_2}{m_1 + m_2} \tag{3.87}$$

The other components of the velocity of the centre of mass are determined in a similar manner, namely,

$$v = \frac{v_1 m_1 + v_2 m_2}{m_1 + m_2} \quad \text{and} \quad w = \frac{w_1 m_1 + w_2 m_2}{m_1 + m_2} \tag{3.88}$$

Let us denote the relative velocity of the molecules by $V$. The components of this velocity, related by the expression

$$V = \alpha^2 + \beta^2 + \gamma^2 \tag{3.89}$$

are obviously the differences between the components of the absolute velocities of the molecules in space, i.e.

$$\begin{aligned} \alpha &= u_2 - u_1 \\ \beta &= v_2 - v_1 \\ \gamma &= w_2 - w_1 \end{aligned} \tag{3.90}$$

Using the notation introduced above, the total kinetic energy of the molecules can be represented as follows:

$$\varepsilon = \frac{1}{2}(m_1 c_1^2 + m_2 c_2^2) = \frac{1}{2}(m_1 + m_2)\,c^2 + \frac{1}{2}\,\frac{m_1 m_2}{m_1 + m_2}\,V^2 \tag{3.91}$$

or introducing the total mass $M$ and the reduced mass $\mu$, in the form

$$\varepsilon = \frac{1}{2} M c^2 + \frac{1}{2}\mu V^2 \tag{3.92}$$

Thus the kinetic energy of two molecules is resolved into two components, one of which is due to the motion of this complex mass in space, and the other to the change in the distance between the molecules. In determining the number of collisions only the second component should obviously be taken into account, since the place of collision is of no difference to us.

We have derived the Maxwell equation (3.62) for the number of molecules travelling in three-dimensional space with velocities ranging from $c$ to $c + dc$. The same equation, when rewritten as follows

$$\frac{dN_V}{N} = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{\mu}{kT}\right)^{3/2} e^{-\mu V^2/2kT} V^2 dV \qquad (3.93)$$

can also be used for calculating the number of pairs of molecules moving with relative velocities ranging from $V$ to $V + dV$. This possibility is connected with the fact that upon randomly selecting

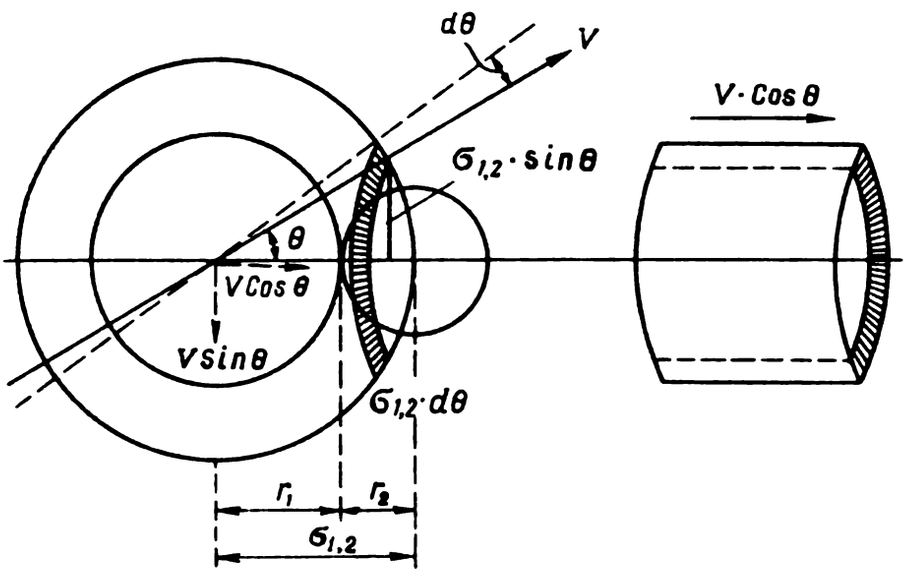


Fig. 3.2. To calculation of frequency of double collisions

any pair of molecules, we can consider one of them to be stationary and the other one travelling with the velocity $V$. We can further find the number of molecules moving relative to the supposedly stationary partners with velocities ranging from $V$ to $V + dV$. This number is given by Eq. (3.93), which in a somewhat different interpretation also expresses the probability of the fact that the randomly selected pair of unlike molecules will have a relative velocity within the indicated limits.

Let us now go over to calculating the frequency of double collisions between molecules of two different species whose concentrations are $n_1$ and $n_2$. Let the radius $r_1$ of molecules of the first species be greater than the radius $r_2$ of molecules of the second species. Let us first find the number of collisions in a unit of time between one molecule of the first species and molecules of the second species, not with any of them, but only with those whose relative velocities are within the limits from $V$ to $V + dV$, and let the angle between the direction of motion of a molecule and the line connecting the centres of the molecules change from $\theta$ to $\theta + d\theta$ (Fig. 3.2).

In general, at the moment of collision the centres of the small molecules should be on the surface of a sphere with a radius of $\sigma_{1,2} = r_1 + r_2$. In view of the condition of limiting the direction

of the relative velocity, however, we consider that the centres of the small molecules at the moment of collision are within the limits of the hatched part of this sphere whose area is equal to $2\pi\sigma_{1,2}\times$ $\times\sin\theta\sigma_{1,2}\,d\theta$. The component of the relative velocity along the line connecting the centres of molecules is equal to $V\cos\theta$, and therefore the volume described by the hatched part in one second will be $2\pi\sigma_{1,2}^2 V\sin\theta\cos\theta\,d\theta$. The number of centres of small molecules arranged in this volume and having velocities ranging from $V$ to $V+dV$ will be equal to the sought number of collisions. Since a unit of volume contains $n_2\frac{dN_V}{N}$ small molecules with the corresponding velocity characteristic, in view of Eq. (3.93) we have

$$dZ=2\pi\sigma_{1,2}^2 V\sin\theta\cos\theta n_2\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{\mu}{kT}\right)^{3/2}e^{-\mu V^2/2kT}V^2\,dV \qquad (3.94)$$

This will be the number of collisions between the small molecules and one large molecule. Since the number of the latter in a unit of volume is $n_1$, the total number of collisions between molecules of both species in a unit of volume in a unit of time will be $n_1$ times greater, i.e.

$$dZ=n_1n_2\sigma_{1,2}^2\pi^{1/2}\left(\frac{2\mu}{kT}\right)^{3/2}e^{-\mu V^2/2kT}V^3\sin\theta\cos\theta\,d\theta\,dV \qquad (3.95)$$

We shall find the total number of collisions, without any limitations, by integration of Eq. (3.95), firstly with respect to $V$ from 0 to $\infty$ and secondly with respect to $\theta$ from 0 to $\pi/2$.

Let us write out separately the values of the corresponding integrals:

$$\int_0^\infty e^{-\mu V^2/2kT}V^3\,dV=\frac{2(kT)^2}{\mu^2}\left|-\left(\frac{\mu V^2}{2kT}+1\right)e^{-\mu V^2/2kT}\right|_0^\infty=\frac{1}{2}\left(\frac{2kT}{\mu}\right)^2$$

$$\int_0^{\frac{\pi}{2}}\sin\theta\cos\theta\,d\theta=\left|\frac{1}{2}\sin^2\theta\right|_0^{\pi/2}=-\frac{1}{2} \qquad (3.96)$$

Thus the total number of collisions of molecules of two different species in a unit of volume in a unit of time will be

$$Z_0=\frac{1}{2}n_1n_2\sigma_{1,2}^2\pi^{1/2}\left(\frac{2\mu}{kT}\right)^{3/2}\frac{1}{2}\left(\frac{2kT}{\mu}\right)^2=$$

$$=n_1n_2\sigma_{1,2}^2\left(\frac{8\pi kT}{\mu}\right)^{1/2}=n_1n_2\sigma_{1,2}^2\left[8\pi kT\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\right]^{1/2} \qquad (3.97)$$

If the colliding molecules are identical, Eq. (3.97) becomes

$$Z_0=\frac{1}{2}n^2\sigma^2\left(\frac{16\pi kT}{m}\right)^{1/2}=2n^2\sigma^2\left(\frac{\pi kT}{m}\right)^{1/2} \qquad (3.98)$$

where $m$ = mass of a molecule
$\sigma$ = diameter of a molecule
$n$ = number of molecules per cubic centimetre.

The factor 1/2 is introduced so as not to take into account the same collisions between identical molecules twice. In addition to the total number of collisions, it is sometimes necessary to know the number of collisions of molecules with the values of the relative velocities limited in some way. For example, let us find $Z_{V_0}$, i.e. the number of collisions of molecules with relative velocities equal to or exceeding a certain value $V_0$. To calculate $Z_{V_0}$, the first of the integrals of Eq. (3.96) should be taken from $V_0$ and the result obtained inserted into Eq. (3.95):

$$\int_{V_0}^{\infty} e^{-\mu V^2/2kT} V^3 dV = \frac{1}{2}\left(\frac{2kT}{\mu}\right)^2 \left(1+\frac{\mu V_0^2}{2kT}\right) e^{-\mu V_0^2/2kT} \tag{3.99}$$

$$Z_{V_0} = n_1 n_2 \sigma_{1.2}^2 \left[8\pi kT\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\right]^{1/2} \times$$
$$\times \left(1+\frac{\mu V_0^2}{2kT}\right) e^{-\mu V_0^2/2kT} = Z_0\left(1+\frac{\mu V_0^2}{2kT}\right) e^{-\mu V_0^2/2kT} \tag{3.100}$$

If we introduce the notation

$$\varepsilon_0 = \frac{1}{2}\mu V_0^2 \tag{3.101}$$

where $\varepsilon_0$ is the relative kinetic energy of the colliding molecules, Eq. (3.100) becomes

$$Z_{\varepsilon_0} = Z_0\left(1+\frac{\varepsilon_0}{kT}\right) e^{-\varepsilon_0/kT} \tag{3.102}$$

and will characterize the frequency of double collisions of molecules with a relative kinetic energy not less than the critical value $\varepsilon_0$. It is very significant that Eq. (3.102) is quite similar to the relation that we would obtain if we simply multiplied the total number of collisions $Z_0$ by the probability of the fact that the participants of the collision have an energy not less than $\varepsilon_0$ (the energy being expressed by four quadratic terms). Indeed, Eq. (3.80) expressing this probability for $2s$ quadratic terms gives us the following factor for $s = 2$:

$$e^{-\varepsilon_0/kT}\left(\frac{\varepsilon_0}{kT}+1\right)$$

which coincides with the factor of $Z_0$ in Eq. (3.102). Hence there follows a simple method for determining the number of double collisions of molecules having an energy equal to or greater than $\varepsilon_0$, but that is expressed by only two quadratic terms ($s = 1$). In other words it makes sense to consider not the total relative velocity $V$

of colliding molecules, but only its component along the line between the centres of the molecules, i.e. $W = V \cos \theta$. The corresponding kinetic energy can be called the relative kinetic energy along the line of centres of molecules. This energy, firstly, is expressed by two quadratic terms, and, secondly, it is this energy that determines the force of a collision and the related magnitude of deformations of the molecules in a collision.

Assuming in Eq. (3.80) that $s = 1$, we get the following expression for the sought frequency of double collisions:

$$Z_{\varepsilon_0} = Z_0 e^{-\varepsilon_0/kT} \qquad (3.103$$

This equation plays a great role in physical chemistry, especially in chemical kinetics. In a particular case, when $\varepsilon_0$ is the relative kinetic energy along the line of centres of molecules, Eq. (3.103) can be written as follows:

$$Z_{W_0} = Z_0 e^{-\mu W_0^2/2kT} \qquad (3.104)$$

where $W_0$ is the critical value of the component of the relative velocity along the line of centres.

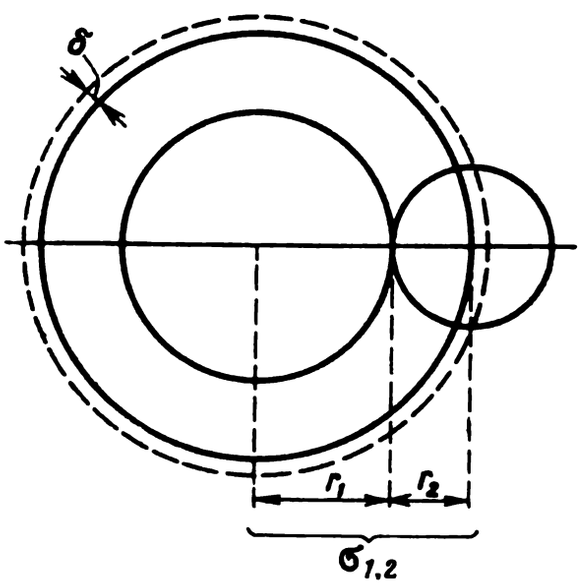


Fig. 3.3. To calculation of frequency of triple collisions

10. *Determining the Frequency of Triple Collisions of Molecules.* The problem of the frequency of triple collisions, i.e. ones in which three molecules simultaneously participate, requires the preliminary determination of the duration of a double collision. The matter is that if we consider molecules as ideal elastic spheres (it is this that underlies the elementary kinetic theory of gases), a double collision is instantaneous, and the probability of a third particle taking part in it is equal to zero. The problem can be solved approximately if we abandon our notion of a double collision as the moment when the centre of a small molecule is on the surface of a sphere with a radius of $\sigma_{1.2} = r_1 + r_2$ (Fig. 3.3) and replace the moment of collision with a finite interval of time during which the centre of the small molecule is in a spherical layer with radii of $\sigma_{1.2}$ and $\sigma_{1.2} + \delta$. Here $\delta$ is an arbitrary quantity, which limits the possibility of quantitative calculations. The mean duration $\tau$ of a double collision determined in this way is equal, as can be shown, to

$$\tau = \delta \left(\frac{2\pi\mu}{kT}\right)^{1/2} \qquad (3.105)$$

The reciprocal of $\tau$ is the probability of the fact that during one second the double complex will break up:

$$\frac{1}{\tau}=\frac{1}{\delta}\left(\frac{kT}{2\pi\mu}\right)^{1/2} \tag{3.106}$$

The volume of a spherical layer with a thickness $\delta$ (Fig. 3.3) is equal to $4\pi\sigma_{1,2}^2\delta$; if a unit of volume contains, say, $n_1$ molecules of the first species, the total volume of all layers with a thickness $\delta$ around all molecules of the first species, equal to $4\pi\sigma_{1,2}^2\delta n_1$, is the probability of the fact that a centre of a molecule of the second species is within the limits of the layer, i.e. that the molecules will collide. If $n_2$ is the number of molecules of the second species in a unit of volume, the number of simultaneously existing double complexes $n_{1,2}$ will be equal to

$$n_{1,2}=4\pi\sigma_{1,2}^2\delta n_1 n_2 \tag{3.107}$$

Reasoning in a similar way, we find for a different pair that the product $4\pi\delta\sigma_{2,3}n_3$ is the probability of collision of a second species molecule with a third species one. Hence we can find the number of triple complexes in one cubic centimetre:

$$n_{1,2,3}=4\pi\sigma_{1,2}^2\,4\pi\sigma_{2,3}\delta^2 n_1 n_2 n_3 \tag{3.108}$$

A triplet stops existing when one of the pairs forming it breaks up; the probability of breaking up of a triplet is equal to the sum of the probabilities of breaking up of the pairs, i.e. according to Eq. (3.106)

$$\frac{1}{\tau}=\frac{1}{\delta}\left(\frac{kT}{2\pi\mu_{1,2}}\right)^{1/2}+\frac{1}{\delta}\left(\frac{kT}{2\pi\mu_{2,3}}\right)^{1/2}$$

In the state of equilibrium the number of triplets formed in a unit of time is equal to the number of complexes breaking up. We shall find the latter number by multiplying the number of triple complexes per cubic centimetre expressed with the aid of Eq. (3.108) by the total probability of breaking up of a complex. We can thus immediately write the number of collisions between molecules of three different species per cubic centimetre per second:

$$Z_{1,2,3}=8\sqrt{2}\,\pi^{3/2}\,n_1 n_2 n_3\sigma_{1,2}^2\sigma_{2,3}^2\delta\,(kT)^{2}\left(\frac{1}{\mu_{1,2}^{1/2}}+\frac{1}{\mu_{2,3}^{1/2}}\right) \tag{3.109}$$

The expression obtained is used in studying trimolecular reactions. It is especially significant that the number of triple collisions is proportional to the product of the concentrations of the three species of colliding molecules.

11. *Determining the Mean Free Path of a Molecule in a Pure Gas.* The number of collisions ($Z$) of one molecule with molecules of the

same species during one second is determined by the relation

$$Z = 2n\sigma^2 \left(\frac{\pi kT}{m}\right)^{1/2}$$

Each collision results in the stopping of the free motion of two molecules. Consequently, the number of free movements discontinued per second will be, when recalculated per molecule, $2Z$. The mean path travelled by a molecule during the same interval of time is determined by its mean velocity [see Eq. (3.52)].

Now we can determine the length of the mean free path:

$$\lambda = \frac{\text{Mean distance covered by molecule per second}}{\text{Number of free movements discontinued per second}} =$$

$$= \frac{\bar{c}}{2Z} = \left(\frac{8kT}{\pi m}\right)^{1/2} \frac{m^{1/2}}{4\pi\sigma^2 (\pi kT)^{1/2}}$$

or

$$\lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2 n} = \frac{0.707}{\pi\sigma^2 n} \tag{3.110}$$

Thus the mean free path of a molecule of an ideal gas is completely determined by the diameter and concentration of the molecules and at the given concentration does not depend on the temperature.

If, finally, we use the equation for an ideal gas $p = nkT$, we get

$$\lambda = \frac{kT}{\sqrt{2}\,\pi\sigma^2 p} \tag{3.111}$$

12. *Determining the Viscosity of an Ideal Gas.* Let us consider an ideal gas moving as a single whole in one direction relative to a fixed system of coordinates, for example in a direction perpendicular to the $x$-axis. The velocity of the mass of the gas as a single whole at different points of space will be different and depend on $x$, i.e. $v = f(x)$, while the change in the velocity $v$ per unit of length along the $x$-axis is determined by the gradient

$$\text{grad}\, v = \frac{dv}{dx} \tag{3.112}$$

It is obvious that together with motion of the gas as a single whole perpendicular to the $x$-axis, molecules move in the gas in all directions with velocities determined by the Maxwell-Boltzmann distribution law.

Let the velocity of the mass of gas in an arbitrarily selected plane $S$ perpendicular to the $x$-axis be equal to a certain value $v$. This means that each molecule in the plane $S$ regardless of the chaotic motion described by the Maxwell-Boltzmann law has an additional component of the velocity in the direction of the motion of the gas as a single whole equal to $v$. Without detracting from the general nature

of our deduction, let us assume for definiteness that the velocity grows to the right of plane $S$ (Fig. 3.4) and diminishes to the left of it. Hence in the right-hand plane $A$ at a distance equal to the free path $\lambda$ from plane $S$ the velocity of the mass of gas will be

$$v_A = v + \lambda \frac{dv}{dx}$$

and at a distance $\lambda$ to the left of plane $S$, in plane $B$

$$v_B = v - \lambda \frac{dv}{dx}$$

$v_A$ being greater than $v_B$. Let us separate on plane $S$ an element with an area $l^2$. The force $F$ acting between planes in which the

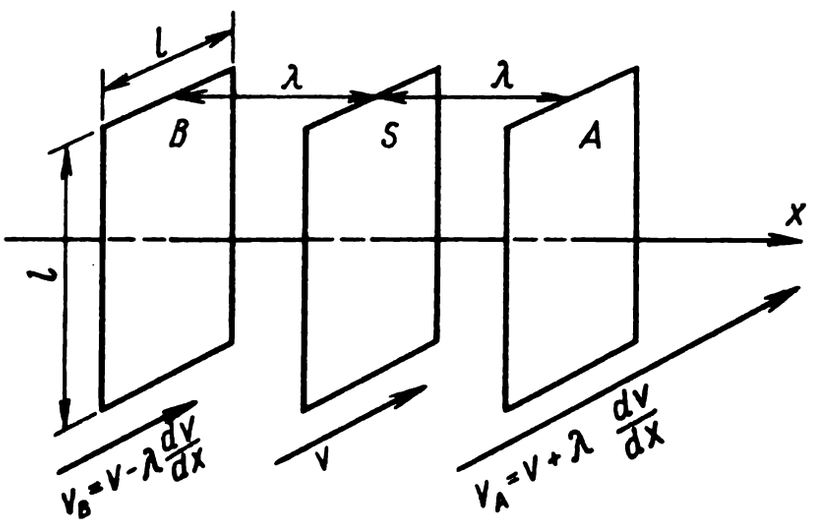


Fig. 3.4. To calculation of viscosity

velocities of the gas are different is, according to I. Newton, directly proportional to the gradient of the velocity and the area of the surface of contact, i.e.

$$F = \eta l^2 \frac{dv}{dx} \tag{3.113}$$

where

$$\eta = \frac{F}{l^2 \frac{dv}{dx}} \text{ g/cm·s} \tag{3.114}$$

is the *coefficient of viscosity* or the *coefficient of friction* of a gas.

During a certain time $t$, surface $S$ will be intersected in the direction from $A$ to $B$ by $nl^2 (kT/2\pi m)^{\frac{1}{2}} t$ molecules of gas [where $n$ is the number of molecules per cubic centimetre, and $(kT/2\pi m)^{\frac{1}{2}}$ is the mean velocity of the molecules in the given direction]. The same number of molecules will intersect plane $S$ in a direction from $B$ to $A$.

Each molecule in plane $A$ has the momentum $m\left(v+\lambda\frac{dv}{dx}\right)$ in the direction of motion of the entire mass of gas. Consequently, during the time $t$ the momentum $p = nml^2\left(\frac{kT}{2\pi m}\right)^{1/2}\left(v+\lambda\frac{dv}{dx}\right)t$ will be transferred from plane $A$ to plane $B$. Correspondingly during the same time $t$ the momentum $-nml^2\left(\frac{kT}{2\pi m}\right)^{1/2}\left(v-\lambda\frac{dv}{dx}\right)t$ will be transferred from plane $B$ to plane $A$. The total momentum transferred during the time $t$ will be $2nml^2\left(\frac{kT}{2\pi m}\right)^{1/2}\lambda\frac{dv}{dx}t$. According to Newton's second law, the derivative of this latter quantity with respect to time will be equal to the acting force, i.e.

$$F = 2nml^2\left(\frac{kT}{2\pi m}\right)^{1/2}\lambda\frac{dv}{dx} \tag{3.115}$$

Inserting Eq. (3.115) into Eq. (3.114), we get

$$\eta = 2nm\left(\frac{kT}{2\pi m}\right)^{1/2}\lambda \tag{3.116}$$

or using Eq. (3.110) for the free path, we have

$$\eta = \frac{1}{\pi^{3/2}}\frac{(mkT)^{1/2}}{\sigma^2} = 0.1792\frac{(mkT)^{1/2}}{\sigma^2} \tag{3.117}$$

# CHAPTER 4

## APPLICATION OF MOLECULAR-KINETIC THEORY TO BIMOLECULAR REACTIONS

**4.1. Effective Diameter of Collision.** The postulate that for the accomplishment of an elementary chemical act the reacting molecules (or other particles, for example atoms, radicals or ions) must collide is absolutely obvious at a first view. Matters, however, are not so simple. The statement on the necessity of a collision in an elementary act completely refutes the possibility of any action at a distance in chemical reactions. Cases are nevertheless possible when, assuming certain geometrical dimensions of the molecules (for example, determined from spectroscopic or electron-diffraction data), we find that although the molecules do not collide geometrically, they react to a certain extent kinetically. Consequently, before unconditionally accepting the postulate of the necessity of a collision in an elementary act, we must define more precisely the purely geometrical (in the first approximation) requirements that must be met by the concept "collision" in chemical kinetics.

If we are considering a bimolecular process of the type

$$A + B \rightarrow \text{Products}$$

the fundamental theoretical formula will be the one characterizing the number of collisions between molecules of species A and species B in a unit of volume in a unit of time [see Eq. (3.97)].

The quantity $\sigma_{AB}$ is called the *collision diameter*. Equation (3.97) is derived for an ideal gas (only specifying that finite dimensions are assigned to the colliding particles), i.e. in the absence of interaction. In this case the value of $\sigma_{AB}$ coincides with that determined by any other methods (for example, by spectroscopic, electron-diffraction, x-ray or other methods). In chemical kinetics, however, we cannot in any way neglect interaction, since it is interaction that is being studied. Therefore, to make the use of Eq. (3.97) possible in studying chemical transformations, the quantity $\sigma_{AB}$ must be determined by a method that to some extent takes into account interaction. If this condition is observed, the quantity $\sigma_{AB,\,eff}$ is called the *effective diameter of collisions*.

For purposes of illustration let us consider the following simplified model (Fig. 4.1). Assume that molecule A is stationary and molecule B is moving in space parallel to a certain fixed straight line

passing through the centre of molecule A. In the absence of interaction (Fig. 4.1*a*) all molecules B whose centres are within a cylinder

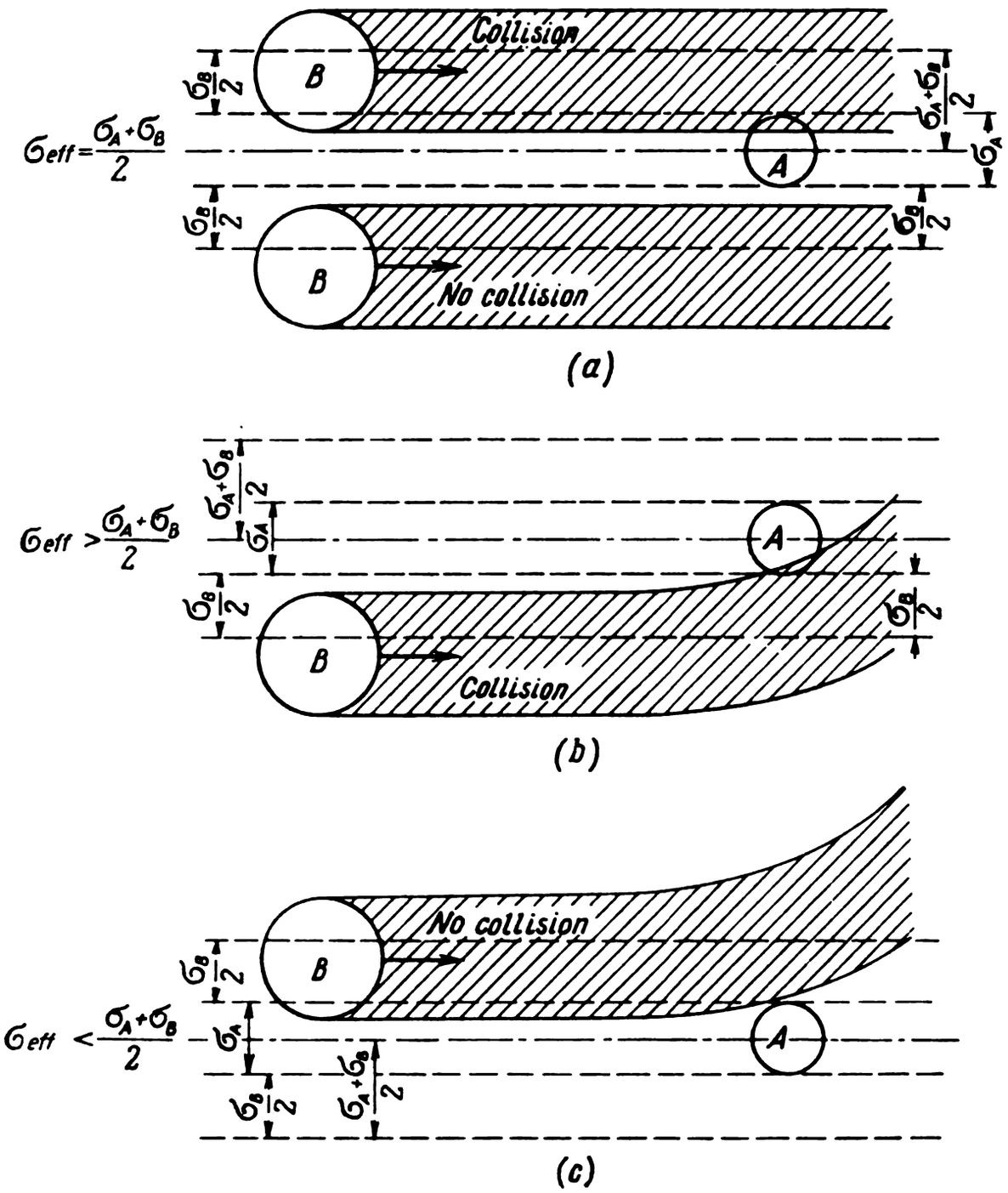


Fig. 4.1. Diagram of possible collisions between two molecules:
*a*—no interaction; *b*—attraction; *c*—repulsion

with the radius $\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$ will collide with molecule A. In this case[1] the effective diameter of collision is equal to the half-sum

[1] This simplified model makes it possible to graphically deduce an approximate formula for the number of collisions between the molecules of one species in one cubic centimetre per second. Indeed, all the molecules having the mean velocity $\bar{c}$ cm/s whose centres are within a cylinder with the volume $\bar{c}\ \pi\sigma^2$ will collide with the stationary molecule during one second, since A and B are iden-

of the diameters of the colliding molecules, namely, $\sigma_{eff} = \frac{\sigma_A + \sigma_B}{2}$. Now let us turn to relations that hold if molecules A and B interact. With attraction, beginning from a certain distance determined by the radius of action of the intermolecular forces, the initially straight paths of the molecules become curved and the molecules begin to approach each other. In the model under consideration this will tell in the curving of the path of molecule B (see Fig. 4.1*b*). As a result of the interaction, part of the molecules B whose centres were originally outside of the cylinder with the radius $\frac{\sigma_A + \sigma_B}{2}$ will collide with molecule A. Obviously, in this case $\sigma_{eff} > \frac{\sigma_A + \sigma_B}{2}$. If repulsion of the molecules occurs, then beginning from a certain distance the paths of the molecules will curve and begin to diverge. In the model being considered this will be expressed in curving of the path of molecule B away from molecule A (Fig. 4.1*c*). Consequently, in repulsion part of the molecules B whose centres were initially in the periphery zone inside the cylinder with the radius $\frac{\sigma_A + \sigma_B}{2}$ will pass molecule A and there will be no collision. In this case we have $\sigma_{eff} < \frac{\sigma_A + \sigma_B}{2}$.

The above example shows that the application of the molecular-kinetic theory of an ideal gas to chemical processes is connected with a number of difficulties. Within the scope of the kinetic theory, two ways of surmounting these difficulties are possible. In one way we can attempt to accept a definite model of the force field of the colliding molecules and deduce all necessary relations on its basis. The types of interaction of particles, however, are sufficiently varied, and for this reason it is difficult to always use the same model. In addition, the analytical relations obtained are difficult to apply, as a rule, to specific calculations owing to their complicated nature or to the necessity of introducing additional parameters.

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tical and $\frac{\sigma_A + \sigma_B}{2} = \sigma$. If there are $n$ molecules in one cubic centimetre, their number in the volume $\bar{c}\pi\sigma^2$ will be $n\bar{c}\pi\sigma^2$. This is the number of collisions of one molecule during one second, and since there are altogether $n$ molecules, the total number of collisions $Z = \frac{1}{2} n^2\bar{c}\pi\sigma^2$, where the factor $\frac{1}{2}$ takes account of the circumstance that none of the $n$ molecules can collide with itself. If we introduce the mean arithmetical value of the velocity $\bar{c} = (8kT/\pi m)^{\frac{1}{2}}$ into this equation, then [see Eq. (3.52)] we get $Z = \sqrt{2}n^2\sigma^2 \left(\frac{\pi kT}{m}\right)^{\frac{1}{2}}$, which differs from the strictly derived relation [see Eq. (3.98)] only in the numerical factor $\sqrt{2} = 1\ 414$.

TABLE 4.1
**Parameters for Calculating the Effective Diameters of Selected Atoms and Molecules**

| Atom or molecule | $\sigma_\infty \times 10^8$, cm | $\frac{\varphi_0}{R}$, deg | Molecule | $\sigma_\infty \times 10^8$, cm | $\frac{\varphi_0}{R}$, deg |
|---|---|---|---|---|---|
| $H_2$ | 2.22 | 234 | $CH_4$ | 3.33 | 162 |
| He | 1.82 | 173 | $C_2H_6$ | 3.88 | 252 |
| Ne | 2.25 | 128 | $C_3H_8$ | 4.46 | 278 |
| Ar | 2.99 | 142 | $n$-$C_4H_{10}$ | 4.58 | 377 |
| $H_2O$ | 2.27 | 961 | $n$-$C_5H_{12}$ | 5.06 | 383 |
| $H_2S$ | 3.18 | 331 | $n$-$C_6H_{14}$ | 5.23 | 436 |
| $SO_2$ | 3.71 | 306 | $CH_2=CH_2$ | 3.72 | 225 |
| NOCl | 3.49 | 500 | $CH_2=CH-CH_3$ | 4.13 | 322 |
| $N_2O$ | 3.25 | 314 | $CH_2=CH-CH_2-CH_3$ | 4.63 | 329 |
| $CO_2$ | 3.45 | 213 | $CH_2=CHCH_2CH_2CH_3$ | 5.22 | 328 |
| COS | 3.73 | 330 | $C_6H_6$ | 4.71 | 448 |
| $CS_2$ | 3.95 | 500 | $C_6H_5CH_3$ | 5.42 | 370 |
| HCN | 2.84 | 901 | $CH_3OH$ | 3.25 | 487 |
| $NH_3$ | 2.47 | 626 | $C_2H_5OH$ | 3.95 | 407 |
| $PH_3$ | 3.45 | 290 | $CH_3Cl$ | 3.57 | 441 |
| $AsH_3$ | 3.59 | 300 | $C_2H_5Cl$ | (4.98) | (366) |

In the second way, if we have an experimentally measured property that depends on the effective diameter of collision, we can use the experimental values of $\sigma_{eff}$. One of these properties (not the only one) is the viscosity, or internal friction of the gas (see Sec. 3.3). The molecular-kinetic theory of an ideal gas gives the following relation between the coefficient of viscosity $\eta$ expressed in g/cm·s and the square of the effective diameter of collision expressed in cm:

$$\sigma_T^2 = 0.1792 \frac{(mkT)^{1/2}}{\eta} \tag{4.1}$$

where $\sigma_T$ is the effective diameter of collision at the temperature $T$.

Since we are dealing with collisions between molecules of the same species, the quantity $\sigma_T$ is also the effective diameter of the given molecules. W. Sutherland proposed a semi-empirical formula for the temperature dependence of $\sigma_T$:[1]

$$\sigma_T^2 = \sigma_\infty^2 \left(1 + \frac{\varphi_0}{RT}\right) \tag{4.2}$$

[1] The correction factor $\left(1 + \frac{\varphi_0}{RT}\right)$ introduced into gas-kinetic formulas for an ideal gas to take approximate account of interaction can be derived for a sphere model of a molecule with a symmetrical central force field. Determination of the temperature dependence of the viscosity is one of the methods of finding the parameter $\varphi_0$ having the dimension of energy.

where $\sigma_\infty$ is the effective diameter at very high (more accurately at $T \to \infty$) temperatures, and the constant $\varphi_0$ has the dimension energy/mol.

Table 4.1 gives the values of the constants $\sigma_\infty$ and $\varphi_0/R$ for selected atoms and molecules determined from measurements of viscosity. They make it possible to calculate the effective diameter of collision at a given temperature. To find the effective diameter of collision for molecules of different species, the half-sum of the values obtained from the data of Table 4.1 for both species should be taken. Concrete examples of such calculations will be given below.

Table 4.2, in addition to the parameters $\sigma_\infty$ and $\varphi_0/R$, compares for diatomic molecules the effective diameters at 298 K with the diameters calculated according to spectroscopic data. There is a certain parallelism between these quantities, namely, $\sigma_{298}$ is approximately equal to 1.5 $\sigma_{spectr}$, which is quite natural.

TABLE 4.2

**Parameters for Calculating the Effective Diameters of Selected Diatomic Molecules and Comparison of the Effective Diameters at 298 K with the Diameters Calculated according to Spectroscopic Data**

| Molecule | $\sigma_\infty \times 10^8$, cm | $\varphi_0/R$, deg | $\sigma_{298} \times 10^8$, cm | $\sigma_{spectr} \times 10^8$, cm |
|---|---|---|---|---|
| $H_2$ | 2.22 | 234 | 2.96 | 1.498 |
| $N_2$ | 3.22 | 105 | 3.75 | 2.18 |
| $O_2$ | 3.02 | 125 | 3.60 | 2.40 |
| $F_2$ | 3.18 | 129 | 3.81 | 2.6 |
| $Cl_2$ | 3.68 | 351 | 5.42 | 3.96 |
| $Br_2$ | 3.80 | 533 | 6.46 | 4.56 |
| $I_2$ | 4.45 | 568 | 7.59 | 5.32 |
| HCl | 2.96 | 362 | 4.42 | 2.54 |
| HBr | 3.16 | 375 | 4.75 | 2.82 |
| HI | 3.55 | 390 | 5.40 | 3.22 |
| NO | 3.09 | 128 | 3.96 | 2.29 |
| CO | 3.23 | 101 | 3.74 | 2.26 |

The method of selecting the value of the effective diameter of collision described in the present section is used in most works on kinetics and can be considered generally accepted. Very great care must be exercised in making conclusions when it becomes necessary to extrapolate data within temperature intervals in which the viscosity was not investigated experimentally.

**4.2. Hypothesis of Active Collisions.** The application of the molecular-kinetic theory to the calculation of the rates of chemical reactions is based on the assumption that every collision leads to the accomplishment of an elementary act. If this assumption is true, the rate of a chemical reaction can be calculated according to the equations for the number of collisions between molecules. Let us check this assumption on the concrete example of the experimentally studied reaction $NOCl + NOCl \rightarrow 2NO + Cl_2$. It has been found experimentally that at 529 K and 760 mm Hg, $1.19 \times 10^{-6}$ mole of nitrosyl chloride decomposes in one cubic centimetre during one second. Since we are dealing with collisions between molecules of one species, the number of collisions can be computed by Eq. (3.98):

$$Z = 2n^2\sigma^2 \left(\frac{\pi kT}{m}\right)^{1/2} = 2n^2\sigma^2 \left(\frac{\pi RT}{M}\right)^{1/2}$$

where $n$ = number of molecules in one cubic centimetre
$M$ = molecular mass.

Using the data of Table 4.1, from Eq. (4.2) we get the following value for the effective diameter of collisions at 529 K:

$$\sigma_{NOCl} = 3.49\sqrt{1+\frac{500}{529}} \times 10^{-8} = 4.87 \times 10^{-8}$$

At 529 K one cubic centimetre contains $\frac{273.2}{22.4 \times 10^3 \times 529} = 2.31 \times 10^{-5}$ mole, or $2.31 \times 10^{-5} \times 6.02 \times 10^{23} = 1.39 \times 10^{19}$ molecules of nitrosyl chloride. Using these data, let us calculate the number of collisions between molecules of nitrosyl chloride in one cubic centimetre during one second:

$$Z = (1.39 \times 10^{19})^2 \times 2 \times (4.87 \times 10^{-8})^2 \sqrt{\frac{3.14 \times 8.314 \times 10^7 \times 529}{65.5}} = 4.14 \times 10^{28}$$

Since (as can be seen from the stoichiometric equation of the reaction) upon each collision two molecules of nitrosyl chloride disappear, during one second $8.28 \times 10^{28}$ molecules or $1.375 \times 10^5$ moles decompose. Let us compare the calculated value of the rate of the reaction $Z$ (the number of collisions) with the value of the rate $Z'$ obtained experimentally:

$$\frac{Z}{Z'} = \frac{1.375 \times 10^5}{1.19 \times 10^{-6}} = 1.21 \times 10^{11}$$

Thus, the calculated rate exceeds the observed one $10^{11}$ times. Such a discrepancy shows that the assumption on the positive outcome of every collision is undoubtedly not correct, and only a small number of collisions between molecules lead to the accomplishment of an elementary act.

The discrepancy between the number of collisions and the number of reacting molecules, and also the experimental dependence of the

rate of a reaction on temperature led S. Arrhenius to a hypothesis according to which only those molecules are capable of entering into a reaction whose energy exceeds a certain critical value. In the Arrhenius equation for the rate constant [see Eq. (1.131)] the constant $E$ has the meaning of this critical quantity, and this constant is generally called the *activation energy*.

At the same time the molecular-kinetic theory gives the following equation for the number of collisions between molecules whose energy exceeds a certain value $E$:

$$Z_a = Z_0 e^{-E/RT} \qquad (4.3)$$

where $Z_0$ is the total number of collisions determined by Eq. (3.97) or (3.98). Combining these two facts, let us state the following assumption: *only those collisions lead to a reaction whose energy exceeds a certain critical value—the activation energy $E$.* This assumption can be verified in two independent ways.

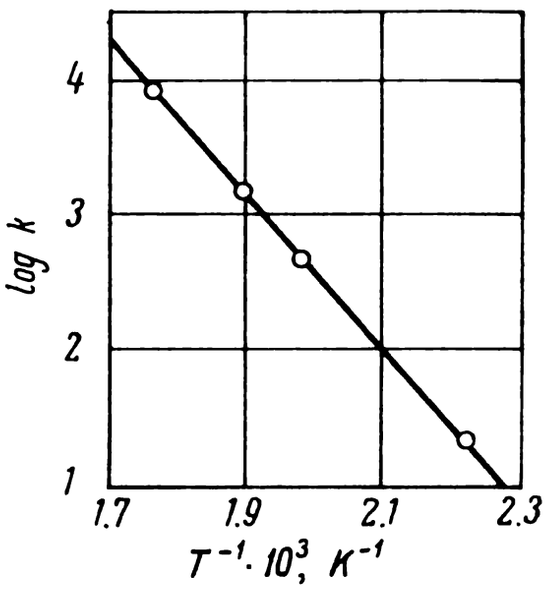



Fig. 4.2. Dependence of log $k$ on $T^{-1}$ for reaction of decomposition of nitrosyl chloride

Firstly, the activation energy can be calculated according to the experimental temperature dependence of the rate constant. By inserting the value obtained into Eq. (4.3), we can obtain the number of active collisions, i.e. those leading to a reaction. The results of comparing this value with the experimental one will show the degree of authenticity of our assumption.

Secondly, the number of active collisions calculated from experimental data can be introduced into Eq. (4.3) and the value of the activation energy can be computed, which is then compared with the one found experimentally.

Let us check the hypothesis of active collisions both ways for the reaction of decomposition of nitrosyl chloride considered above.

*First way.* Figure 4.2 shows the experimental dependence of log $k$ on the inverse temperature $T^{-1}$. The tangent of the angle of inclination gives us the value of $E$ = 26 000 cal/mol. Hence, according to Eq. (4.3) the number of active collisions

$$Z_a = 4.14 \times 10^{28} e^{-\frac{26\,000}{1.987 \times 529}} = 4.14 \times 10^{28} e^{-24.5} = 1.048 \times 10^{18}$$

and in one cubic centimetre

$$\frac{2 \times 1.048 \times 10^{18}}{6.02 \times 10^{23}} = 3.48 \times 10^{-6} \text{ mol}$$

should decompose during one second.

Let us compare the value obtained with the experimental one:

$$\frac{Z}{Z'} = \frac{3.48 \times 10^{-6}}{1.19 \times 10^{-6}} \cong 3$$

*Second way*. The experimental number of collisions leading to a reaction is equal to

$$Z' = 1.19 \times 10^{-6} \frac{6.02 \times 10^{23}}{2} = 3.58 \times 10^{17}$$

Inserting this value into Eq. (4.3), we get

$$3.58 \times 10^{17} = 4.14 \times 10^{23} e^{-\frac{E}{1.987 \times 529}}$$

whence the value of the activation energy is

$$E = 4.575 \times 529 \, [\log (4.14 \times 10^{11}) - \log (3.58)] = 26\,750 \text{ cal/mol}$$

This value differs from the one found experimentally by less than 3%.

The results obtained in both ways show that the hypothesis of active collisions is confirmed by experimental data, since the discrepancies are within the scope of possible errors in the experiments and are also due to the arbitrary nature of determining $\sigma_{eff}$.

For many reactions, for example the synthesis and decomposition of hydrogen iodide, the interaction of methyl iodide with hydrogen iodide, ethyl iodide with hydrogen iodide and a number of others, satisfactory coincidence of the theoretical and experimental values is observed. More frequently, however, the calculated value exceeds the experimental one (they differ by a certain constant number of times). Let us consider, for example, the reaction $NO_2 + NO_2 \rightarrow 2NO + O_2$. At 625 K and 760 mm Hg, $6.37 \times 10^{-7}$ mole of nitrogen dioxide react in one cubic centimetre per second (according to experimental data). Therefore, the number of active collisions is $\frac{1}{2}(6.02 \times 10^{23} \times 6.37 \times 10^{-7}) = 1.917 \times 10^{17}$. The activation energy determined graphically from the relation $\log k = f(T^{-1})$ is equal to 26 500 cal/mol. Let us assume that the effective diameter is equal to $3.5 \times 10^{-8}$ cm (no accurate data are available for calculating the value of $\sigma_{eff}$ for nitrogen dioxide). Consequently, the calculated number of active collisions will be

$$Z_a = 2(1.951 \times 10^{-5} \times 6.02 \times 10^{23})^2 (3.5 \times 10^{-8})^2 \times$$

$$\times \left(\frac{8 \times 3.14 \times 8.314 \times 10^7 \times 625}{46}\right) \times e^{-\frac{26\,500}{1.987 \times 625}} = 1.105 \times 10^{19}$$

Comparison of experiment and theory gives

$$\frac{Z'}{Z} = \frac{1.917 \times 10^{17}}{1.105 \times 10^{19}} = 1.73 \times 10^{-2}$$

This discrepancy can no longer be explained by errors in experiment or improper selection of the value of $\sigma_{eff}$. In particular, for the calculated and experimental values to coincide, it would be necessary to assume that

$$\sigma_{eff} = 3.5 \times 10^{-8} \sqrt{\frac{1.917 \times 10^{17}}{1.105 \times 10^{19}}} = 4.6 \times 10^{-9} \text{ cm}$$

which obviously has no physical meaning.

Consequently, the deviation of the calculated values from the experimental ones has a significance of principle and shows that a chemical reaction is not absolutely authentic upon an active collision, but has a finite probability equal to $P$. There may be several reasons for this. Let us meanwhile consider two of them.

Firstly, for complex molecules there must be such an arrangement of the active groups in an active collision that would ensure the formation of the products. The probability of the corresponding geometrical configuration in collision gives the value of $P$, which is called the *steric factor*.

Secondly, in the theory set out above it is assumed that before the critical energy is reached in a collision, the reaction will not proceed, and after this energy is reached it will proceed regardless of how much the value of $E$ is exceeded. An elementary act may also occur, however, at values of the collision energy less than $E$ (the tunnel effect), and the probability of the reaction may grow as the energy of the colliding molecules increases in comparison with the activation energy.

The theory of activated complexes, which will be considered in the following chapter, gives methods of calculating the steric factor $P$ with the aid of the molecular parameters of the reacting system.

**4.3. Application of Collision Theory to Bimolecular Reactions. Calculation of Rate Constant.** On the basis of the molecular-kinetic theory and the hypothesis of active collisions, we can give the following theoretical interpretation of a bimolecular reaction of the type

$$A + B \rightarrow \text{Products}$$

An elementary act occurs only when reacting particles collide. If the total energy of the colliding molecules[1] is less than a certain critical value $\varepsilon_a$, the probability of a reaction vanishes. If the total energy of the colliding molecules is equal to $\varepsilon_a$ or greater than this critical value to any extent, the probability of reaction is equal to a finite quantity $P$. Hence, according to the statement made and

[1] More exactly, the total kinetic energy of relative motion of the molecules along the line of their centres. Consequently, only two degrees of freedom of translational motion of the molecules are taken into account.

to Eqs. (3.97) and (4.3), the rate of the reaction (in molecules/cm$^3$·s) can be written as follows:

$$-\frac{dn_A}{dt} = PZ_a = Pn_A n_B \sigma_{AB}^2 \left[ 8\pi kT \left( \frac{1}{m_A} + \frac{1}{m_B} \right) \right]^{1/2} e^{-\varepsilon_a/kT} \quad (4.4)$$

This relation is the fundamental mathematical expression of the theory of collisions for bimolecular reactions. Various practically applicable forms and a relation between the rate constant and molecular parameters of the reacting system can be obtained from it. If the concentrations of the reacting molecules are expressed in mol/cm$^3$, i.e.

$$c_A = \frac{n_A}{N} \quad \text{and} \quad c_B = \frac{n_B}{N} \quad (4.5)$$

then Eq. (4.4) becomes

$$-\frac{d\frac{n_A}{N}}{dt} = -\frac{dc_A}{dt} = P\frac{Z_a}{N} = Pc_A c_B N \sigma_{AB}^2 \left[ 8\pi kT \left( \frac{1}{m_A} + \frac{1}{m_B} \right) \right]^{1/2} e^{-\varepsilon_a/kT} \quad (4.6)$$

At the same time for the bimolecular reaction being considered, the main postulate of chemical kinetics gives

$$-\frac{dc_A}{dt} = k_r c_A c_B \quad (4.7)$$

A comparison of Eqs. (4.6) and (4.7) gives a theoretical expression for the rate constant of a bimolecular reaction:

$$k_r = P\sigma_{AB}^2 N \left[ 8\pi kT \left( \frac{1}{m_A} + \frac{1}{m_B} \right) \right]^{1/2} e^{-\varepsilon_a/kT} \quad (4.8)$$

When the molecular parameters are expressed in molar quantities, Eq. (4.8) becomes

$$k_r = PN\sigma_{AB}^2 \left[ 8\pi RT \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2} e^{-E_a/RT} \quad (4.9)$$

or, combining constant quantities in the preexponential factor, i.e.

$$N\sigma_{AB}^2 \left[ 8\pi R \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2} = C \quad (4.10)$$

called the *collision factor*, we have

$$k_r = PC\sqrt{T}\, e^{-E_a/RT} \quad (4.11)$$

After taking logarithms, Eq. (4.11) becomes

$$\ln k_r = \ln (PC) + \frac{1}{2} \ln T - \frac{E_a}{RT} \quad (4.12)$$

Differentiation of Eq. (4.12) gives

$$\frac{d \ln k_r}{dT} = \frac{E_a + \frac{1}{2} RT}{RT^2} \tag{4.13}$$

Comparing Eq. (4.13) with the Arrhenius equation, we get

$$E = E_a + \frac{1}{2} RT \tag{4.14}$$

Since most chemical reactions are conducted at temperatures up to 1000 K, and the activation energy is of the order of $10^4$-$10^5$ cal/mol, the quantity $\frac{1}{2} RT \approx T \leqslant 1000$ cal/mol may be neglected, and Eq. (4.13) written as

$$\frac{d \ln k_r}{dt} = \frac{E}{RT^2} \tag{4.15}$$

or

$$k_r = Ce^{-E/RT} \tag{4.16}$$

which coincides with the Arrhenius equation. It is clear from what has been said above that the use of Eq. (4.16) is justified at sufficiently high activation energies ($E \gg RT$). If this condition is not observed, the more accurate equation (4.13) should be used.

**4.4. Maxwell-Boltzmann Distribution in Reacting System. Activation Energy.** In the course of a chemical reaction the number of active molecules, transforming into products, continuously diminishes. If the rate of a reaction is considerably lower than that of molecular-kinetic activation, the relative number of active molecules will remain constant and the Maxwell-Boltzmann distribution will not be distorted. If the reaction proceeds sufficiently rapidly and its rate is comparable with the rate of activation, the relative number of active particles will diminish, i.e. so-called *burning out of active particles* will occur. This phenomenon is of great importance for the interpretation of rapid processes such as explosive and branching-chain ones.

For reactions whose rate can be measured by ordinary methods, the following criterion is possible for showing how the number of active particles in a reacting system agrees with the Maxwell-Boltzmann distribution. If the activation energy is sufficiently great, the number of active particles forms an insignificant part of all the particles in the system. Their negligible decrease in the course of the reaction will easily be replenished as a result of activation upon collisions. If the activation energy is small, a considerable part of the particles are capable of reacting, and the Maxwell-Boltzmann distribution will no longer have time to restore as the

result of collisions. Thus, a practically convenient criterion of observance of the Maxwell-Boltzmann distribution during a reaction is the inequality

$$E \gg RT \ (\varepsilon_a \gg kT) \tag{4.17}$$

Inequality (4.17) shows that at a given activation energy any process, when the temperature grows, can pass over into the region of non-observance of the Maxwell-Boltzmann distribution.

According to the latter, the number of collisions $Z_{\varepsilon_i}$ whose energy is equal to a certain value $\varepsilon_i$ is

$$Z_{\varepsilon_i} = \frac{Z_0 e^{-\varepsilon_i/kT}}{\sum\limits_0^\infty e^{-\varepsilon_i/kT}} \tag{4.18}$$

where $Z_0$ is the total number of collisions.

Let us now renounce the assumption according to which the probability of reaction is constantly independent of the excess energy of collisions in comparison with the activation energy, and let us consider that a definite value of the rate constant $k_{\varepsilon_i}$ corresponds to each value of the collision energy $\varepsilon_i$. Hence, assuming that the rate constant is expressed in $cm^3/s$, we get the following expression for a collision with the energy $\varepsilon_i$:

$$k_{\varepsilon_i} = \frac{Z_0 e^{-\varepsilon_i/kT}}{\sum\limits_0^\infty e^{-\varepsilon_i/kT}} \tag{4.19}$$

On the basis of Eq. (4.19), if we neglect the tunnel effect, we obtain the observed total rate constant:

$$k_r = \sum_0^\infty k_{\varepsilon_i} = \frac{Z_0 \sum\limits_{\varepsilon_a}^\infty e^{-\varepsilon_i/kT}}{\sum\limits_0^\infty e^{-\varepsilon_i/kT}} \tag{4.20}$$

After taking logarithms and differentiating Eq. (4.20) we have[1]

$$\frac{d \ln k_r}{dT} = \frac{1}{kT^2} \frac{\sum\limits_{\varepsilon_a}^\infty \varepsilon_i e^{-\varepsilon_i/kT}}{\sum\limits_{\varepsilon_a}^\infty e^{-\varepsilon_i/kT}} - \frac{1}{kT^2} \frac{\sum\limits_0^\infty \varepsilon_i e^{-\varepsilon_i/kT}}{\sum\limits_0^\infty e^{-\varepsilon_i/kT}} \tag{4.21}$$

---

[1] In differentiation $Z_0$ is considered constant, i.e. the addend $\frac{d \ln Z_0}{dT} = \frac{1}{2T}$ is discarded.

The first addend is the mean energy of active collisions $\bar{\varepsilon}_a = \bar{E}_a/N$ and the second the mean energy of all the collisions $\bar{\varepsilon} = \bar{E}/N$. Thus

$$\frac{d \ln k_r}{dT} = \frac{\bar{E}_a - \bar{E}}{RT^2} \tag{4.22}$$

Comparison of Eq. (4.22) with Eq. (4.15) shows that *the activation energy is the difference between the mean energy of active collisions and the mean energy of all collisions.* The above definition of the activation energy is the strictest one within the scope of application of the molecular-kinetic theory to the investigation of rates of chemical reactions. A different interpretation of the activation energy will be given in considering the theory of the activated complex.

**4.5. Types of Bimolecular Reactions.** Above we described cases when an elementary act is accomplished more easily on a solid surface than in a bulk. Taking this into account, we can assume that many homogeneous reactions are made more complicated by heterogeneous stages on the walls of the vessel in which the process being investigated proceeds. For example, at room temperature the reaction of decomposition of ozone is heterogeneous with a comparatively low activation energy and proceeds on the walls of the vessel. With an elevation of the temperature, a purely homogeneous process with an activation energy of about 24 000 cal/mol begins to play a greater and greater role, and within the temperature range from 60 to 100 °C its rate exceeds that of heterogeneous decomposition to such an extent that the observed experimental value of the reaction rate completely characterizes a homogeneous process. Similar phenomena are also observed in many other instances, for example in the decomposition of gaseous hydrides of elements of group V ($NH_3$, $PH_3$, $AsH_3$, $SbH_3$) of the periodic table.

To experimentally find the influence of heterogeneous reactions on the course of a process, it is the best practice to use the following procedure. Fill the vessel in which the experiment is being conducted with finely crushed pieces of the material its walls are made of. The surface thus increases hundreds of thousands and millions of times. If the rate of the reaction and its kinetic characteristics remain unchanged, the reaction being investigated can be considered to be a purely homogeneous one. Otherwise additional investigations must be conducted to determine the role played by the solid surface.

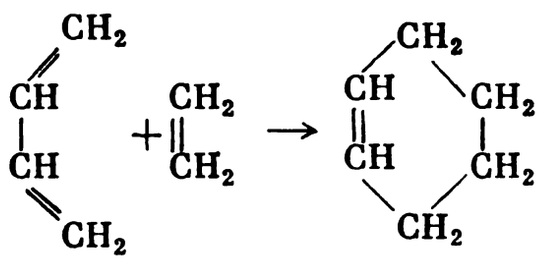
Bimolecular reactions are the most widespread class of chemical transformations. Before free radicals were identified and kinetically studied, purely bimolecular homogeneous reactions in a gaseous phase seemed to be rare, and the synthesis and decomposition of hydrogen iodide was almost the only standard example. After the separate stages of chemical transformations became the subject of direct experimental investigation, it was found that most complicated reactions can be represented in the form of elementary stages or

steps which in their predominating majority are bimolecular elementary acts. In addition, since the process of activation is a bimolecular one, it was found that monomolecular reactions also pass through a bimolecular stage. The accumulated data make it possible to divide all bimolecular reactions into three types.

1. *Reactions between Valence-Saturated Molecules.* These are reactions of exchange, for example

$$HI + C_2H_5I \rightarrow C_2H_6 + I_2$$

or association, for example



Their feature is that the number of free valences before and after a reaction is equal to zero.

2. *Reactions of a Radical (or Atom) with a Valence-Saturated Molecule.* Reactions of this type include most of the intermediate steps of complicated reactions. In such reactions, for example

$$CH_3^{\bullet} + C_2H_6 \longrightarrow CH_4 + C_2H_5^{\bullet}$$

or

$$H\bullet + CH_2{=}CH_2 \longrightarrow CH_3{-}CH_2^{\bullet}$$

the free valence in the reactants also remains in the products, or the number of free valences grows, for example

$$H\bullet + O_2 \longrightarrow OH\bullet + O.$$

Such processes are of a great significance for the proceeding of branching chain reactions.

3. *Recombination of Atoms and Radicals.* In the recombination of radicals the free valences of the reactants disappear and a saturated molecule is formed. Processes of such a type are only slightly probable from energy considerations, and recombination most frequently occurs on walls or in a triple collision. With a growth in the number of atoms in a radical, however, the possibility of redistribution of the energy among the internal degrees of freedom grows and bulk reactions of the type

$$CH_3^{\bullet} + C_2H_5^{\bullet} \longrightarrow C_3H_8$$

can successfully compete with recombinations of the two other types.

**4.6. Bimolecular Reactions between Valence-Saturated Molecules.** Table 4.3 gives data on certain bimolecular reactions between valen-

TABLE 4.3

**Selected Bimolecular Reactions between Valence-Saturated Molecules**

| Reaction | Temperature interval, K | Rate constant, $cm^3/mol \cdot s$ | $P$ |
|---|---|---|---|
| $H_2 + I_2 \rightarrow 2HI$ | 556-781 | $3.62 \times 10^{12} \sqrt{T}\, e^{-39\,000/RT}$ | 0.1 |
| $HI + HI \rightarrow H_2 + I_2$ | 556-781 | $3.32 \times 10^{12} \sqrt{T}\, e^{-44\,000/RT}$ | 1 |
| $HI + CH_3I \rightarrow CH_4 + I_2$ | 523-583 | $8.5 \times 10^{12} \sqrt{T}\, e^{-33\,400/RT}$ | 0.6 |
| $HI + C_2H_5I \rightarrow$ $\rightarrow C_2H_6 + I_2$ | 523-583 | $2.1 \times 10^{12} \sqrt{T}\, e^{-29\,800/RT}$ | 0.13 |
| $NOCl + NOCl \rightarrow$ $\rightarrow 2NO + Cl_2$ | 451-567 | $3.83 \times 10^{12} \sqrt{T}\, e^{-26\,000/RT}$ | 1 |
| $NO_2 + NO_2 \rightarrow$ $\rightarrow 2NO + O_2$ | 592-656 | $1.25 \times 10^{11} \sqrt{T}\, e^{-26\,500/RT}$ | 0.02 |

ce-saturated molecules. Here two facts attract attention, namely, the activation energies are quite high (30 000-40 000 cal/mol), and the steric factors vary from 1 to $2 \times 10^{-2}$. The former circumstance is easy to explain. For achieving a reaction, a bond must be broken in at least one of the reacting molecules, and, consequently, the activation energy should be commensurable with the bond energy. The comparative closeness of the steric factors to unity shows that the redistribution of the bonds upon a collision essential for the proceeding of the reaction, if the energy of the collision is sufficiently high, can be geometrically achieved quite easily. It is probably for this reason that bimolecular reactions usually proceed between molecules having a comparatively simple structure and composition. In the interaction of more complicated molecules, the possibility of redistribution of the energy between the internal degrees of freedom appears. This may lead to kinetic complications, while the complication of the geometrical conditions of the resulting collision and the intricate order of redistribution of the bonds reduce the numerical value of the steric factor $P$.

**4.7. Reactions with Participation of Radicals.** The probability of the bulk bimolecular recombination of atoms and the simplest radicals is low, and the small values of the steric factors (for example, for the recombination of atomic hydrogen of the order of $10^{-14}$, for the recombination of atomic halogens of the order of $10^{-7}$, etc.) correspond to this circumstance. This is notwithstanding the fact

TABLE 4.4
**Selected Reactions with the Participation of Valence-Unsaturated Particles**

| Reaction | Rate constant, $cm^3/mol \cdot s$ | $P$ |
|---|---|---|
| $H + H_2 \rightarrow H_2 + H$ | $5.03 \times 10^{12} \sqrt{T}\, e^{-8500/RT}$ | 0.86 |
| $H + C_2H_6 \rightarrow H_2 + C_2H_5\cdot$ | $3.5 \times 10^{12} \sqrt{T}\, e^{-6800/RT}$ | 0.055 |
| $H + C_2H_2 \rightarrow C_2H_5\cdot$ | $6.3 \times 10^{11} \sqrt{T}\, e^{-1500/RT}$ | 0.03 |
| $O + H_2 \rightarrow OH\cdot + H$ | $1.2 \times 10^{11} \sqrt{T}\, e^{-16\,000/RT}$ | 0.07 |
| $OH\cdot + H_2 \rightarrow H_2O + H$ | $4.48 \times 10^{12} \sqrt{T}\, e^{-10\,000/RT}$ | 0.57 |
| $OH\cdot + C_2H_6 \rightarrow H_2O + C_2H_5\cdot$ | $6.58 \times 10^{12} \sqrt{T}\, e^{-5500/RT}$ | 0.66 |
| $CH_3\cdot + C_2H_6 \rightarrow CH_4 + C_2H_5\cdot$ | $2.14 \times 10^{11} \sqrt{T}\, e^{-10\,400/RT}$ | 0.0005 |
| $CH_3\cdot + C_2H_4 \rightarrow CH_4 + C_2H_3\cdot$ | $2.09 \times 10^{11} \sqrt{T}\, e^{-10\,000/RT}$ | 0.0005 |
| $HO_2\cdot + H_2O \rightarrow H_2O_2 + OH\cdot$ | $3 \times 10^{11} \sqrt{T}\, e^{-30\,000/RT}$ | — |

that all these processes proceed with an activation energy equal to or close to zero.

Reactions with the participation of a radical or atom, on the contrary, are the most widespread type of chemical elementary act. Table 4.4 gives selected examples of reactions of this type. They are all characterized by a low (not over 10 000 cal/mol) value of the activation energy. A greater value of the activation energy has been obtained only for the radical $HO_2^{\cdot}$ having a low activity, whose properties are close to those of a saturated molecule. This is quite obvious, since the presence of a free valence in the initial system facilitates the accomplishment of the reaction from the energy viewpoint. For the same reason a linear relation between the activation energy and the heat of reaction is observed for many reactions with the participation of radicals. After considering an appreciable number of reactions, N. Semenov proposed to assume for exothermic reactions

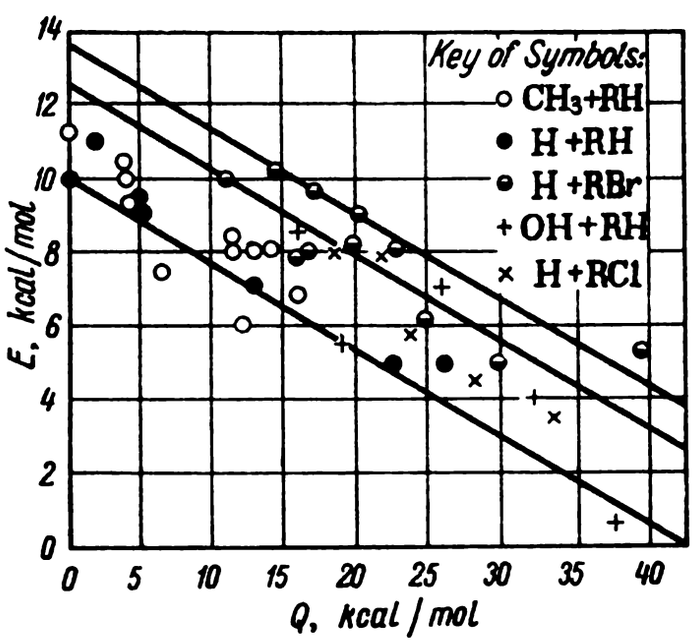



Fig. 4.3. Relation between activation energy $E$ and heat of reaction $Q$ for exothermic reactions

$$E = 11\,500 - 0.25\bar{Q} \tag{4.23}$$

and for endothermic ones

$$E = 11\,500 + 0.25\bar{Q} \tag{4.24}$$

The correctness of these relations is illustrated by a number of reactions (Fig. 4.3).

The high reactivity of atoms and radicals can be well illustrated on the example of a reaction with the participation of atomic oxygen. Thus, reacting with methane, atomic oxygen replaces two atoms of hydrogen, as a result of which formaldehyde is formed:

$$O + CH_4 \rightleftarrows CH_2O + H_2$$

The oxygen can enter the molecule along the bond C—H, and as a result methyl alcohol is formed:

$$O + CH_4 \rightleftarrows CH_3OH$$

Atomic oxygen oxidizes formaldehyde to produce carbon monoxide and water:

$$O + CH_2O \rightleftarrows CO + H_2O$$

and, finally, with the participation of a third particle oxidizes CO to $CO_2$:

$$O + CO + M \rightleftarrows CO_2 + M$$

The addition of radicals to molecules with a multiple bond proceeds, as a rule, at low values of the activation energy. Thus, the formation of the radical $HO_2^{\cdot}$

$$H + O_2 \rightleftarrows HO_2^{\cdot}$$

proceeds with an activation energy close to zero. The reactions

$$H + CH_2{=}CH_2 \longrightarrow CH_3{-}CH_2^{\cdot} \quad \text{and} \quad CH_3^{\cdot} + CH_2O \longrightarrow C_2H_5O^{\cdot}$$

are possible at an activation energy of only 7000 cal/mol, etc. The steric factors vary (depending on the complicacy of the interacting particles) from values close to unity to values of the order of $10^{-5}$.

**4.8*. Reactions in Rarefied Flames.** This term denotes an interesting class of radical reactions of interaction of alkali metal atoms with halogen molecules. All the elementary steps and the mechanism of chemiluminescence have been determined for these reactions with a sufficient degree of accuracy. They proceed at pressures of the order of $10^{-1}$ to $10^{-3}$ mm Hg within the temperature range from 200 to 300 °C. The vapours of both reactants are mixed in a long reaction tube. The products are deposited on the walls of the tube, which makes their analysis possible. The reaction is accompanied by intensive chemiluminescence—the emission of light due to the presence of electrically excited atoms of a metal during the chemical reaction. All the processes are bimolecular, since triple collisions at such low pressures have a low probability. The low temperatures and the absence of an explicit temperature dependence of the reaction rate show that the activation energies are low or equal to zero.

Let us consider as an example the reaction of interaction of atomic sodium with molecules of iodine. There are two zones in the reaction tube along its length, namely, (1) a zone of formation of the greatest amount of the product, NaI (closer to the inlet of the stream of molecular iodine), and (2) a zone of the most intensive light emission at the expense of the energy of the process

$$Na^{*} \rightarrow Na + h\nu$$

The main process of formation of NaI proceeds in the first zone:

$$I_2 + Na \rightarrow NaI + I + 33\ 700 \text{ cal/mol}$$

Its energy is insufficient for exciting chemiluminescence, since the wavelengths of the double $D$-line of sodium are equal to 5889.96 and 5895.93 Å, which approximately corresponds to 48 300 cal/mol. The iodine atom formed can combine with an atom of sodium:

$$I + Na \rightarrow NaI + 68\ 500 \text{ cal/mol}$$

But since the probability of stabilization by a triple collision is very low, such a process can proceed only on the walls, and its part in the total balance is negligible.

In the second zone the concentration of molecular sodium is quite considerable. The equilibrium constant of the reaction $Na + Na \rightleftarrows Na_2$ is

$$K_{200\ °C} = \frac{p_{Na_2}}{p_{Na}^2} = 0.085$$

Consequently, the process

$$I + Na_2 \rightleftarrows NaI + Na + 49\ 500 \text{ cal/mol}$$

is quite possible, and chemiluminescence occurs at the expense of its energy.

CHAPTER 5

# THEORY OF ACTIVATED COMPLEX (TRANSITION STATE)

**5.1. Surface of Potential Energy. Activated Complex. Coordinate and Path of Reaction.** Let us consider the reaction of an atom Z with a diatomic molecule XY according to the reaction $XY + Z \rightleftarrows X + YZ$.

As atom Z approaches molecule XY along the straight line connecting the nuclei of atoms X and Y, the bond between atoms Z and Y becomes stronger, and between atoms X and Y weaker. At a certain distance between atom Z and molecule XY an intermediate state appears when a so-called *activated complex* (or *transition state*) X-Y-Z is formed. The latter decomposes to form the products: free atom X and molecule YZ.

Approximate quantum-chemical calculations show that the minimum energy is spent when atom Z approaches molecule XY as considered above. To watch the change in the potential energy of a system of three atoms in the course of the reaction, let us plot a diagram in Cartesian coordinates, laying off the distance $r_{X-Y}$ between atoms X and Y along the axis of abscissas and the distance $r_{Y-Z}$ between atoms Y and Z along the axis of ordinates on condition that the valence angle of the activated complex X-Y-Z is fixed and equal to 180 degrees (Fig. 5.1)[1]. The magnitude of the energy is laid off in the diagram along an axis perpendicular to the plane of the drawing similar to the way the relief of a locality is shown on a topographical map by contour lines. The solid lines show levels of equal energy expressed in kilocalories. The change in the potential energy can be watched according to the isoenergy lines (equal energy contour lines) on the energy surface projected onto the plane $r_{X-Y}$-$r_{Y-Z}$.

Continuing the analogy with the relief of a locality, it is easy to conceive with the aid of the diagram in Fig. 5.1 that the potential energy surface will have two valleys (corresponding to the sections shown at the top and the right of the diagram) separated by a ridge or pass. The lowest point of this pass is indicated in the figure by a cross.

When atom Z is far from molecule XY (the top left-hand corner of the diagram), the potential energy of the system consisting of

[1] If this condition is not observed, then calculations show that it is convenient to use an oblique-angled system of coordinates.

three atoms mainly depends on the interatomic distance $r_{X-Y}$, and this relation can be described by the curve of the potential energy of the diatomic molecule XY shown in the upper part of the diagram. As atoms Z and Y approach each other, the interaction between them

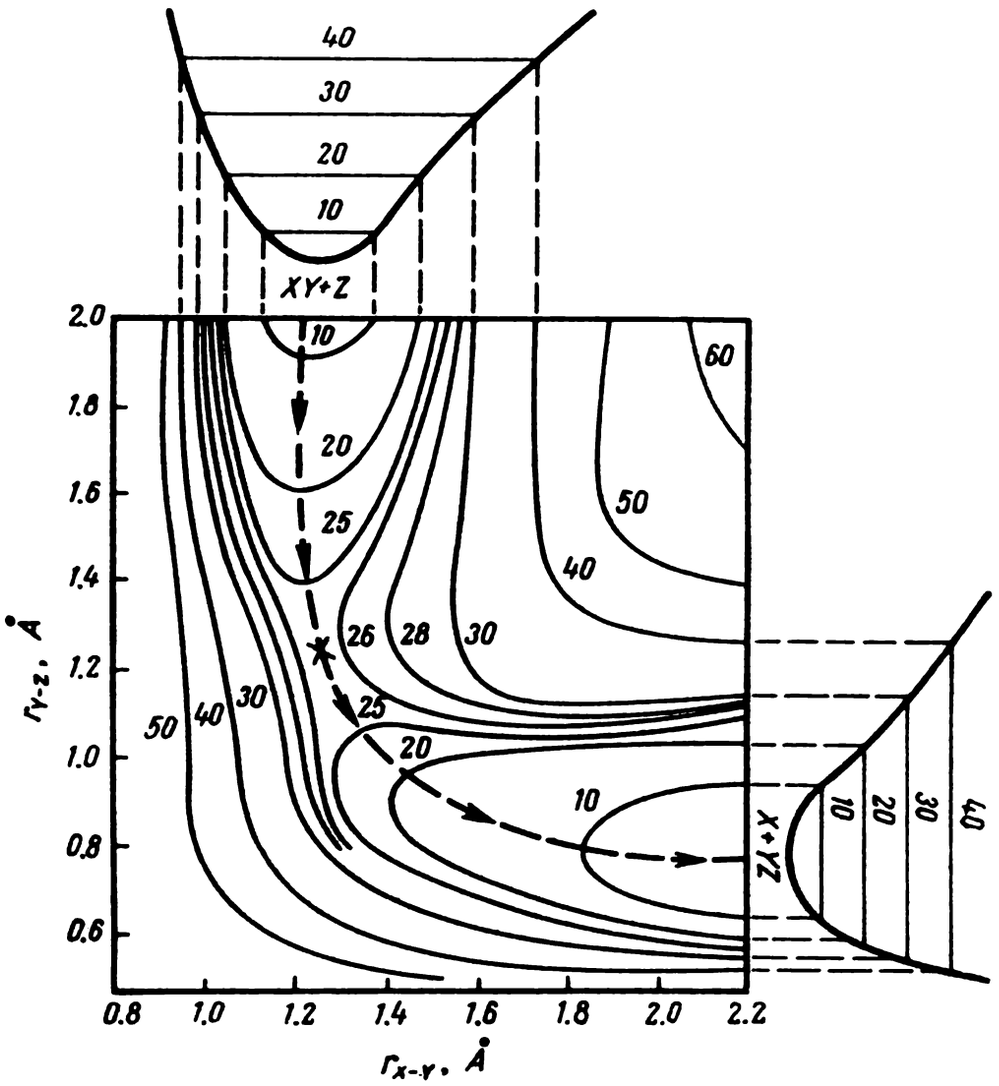



Fig. 5.1. Change in potential energy of system for reaction of type XY + Z → → X + YZ

begins to tell, the bond X—Y weakens owing to the increase in the distance between X and Y, and a new bond Y—Z begins to appear. Here, as can be seen from the diagram, the potential energy of the system grows, and at a certain point (shown by a cross in the diagram) reaches a maximum. In the state corresponding to this point the molecules XY or YZ no longer exist separately. At the moment when the system of three atoms passes the maximum of the potential energy it forms a certain integral complex similar in its properties to an unstable triatomic molecule. This state has been named the *activated complex*, or the *transition state*. When atoms Z and Y continue to approach each other, the bond Z—Y becomes stronger, atom X separates from atom Y, the potential energy of the system

begins to diminish, and then the system passes into its final state. Here a stable molecule YZ is formed whose potential energy is shown by the curve at the right of the diagram, and a free atom X.

An attentive examination of Fig. 5.1 will show that the most probable state of the system (when the interatomic distances $r_{X-Y}$ and $r_{Y-Z}$ change) passes along an energy "valley", then over the "saddle" point and down along another "valley" to the final state. The combination of the most probable states of a system is called the *reaction path* (shown in Fig. 5.1 by a thick dotted line).

The diagram described above obviously gives a detailed energy picture of the active collisions considered in Chapter 4. The difference between the potential energy of the reactants and that at the top of the barrier is the energy of activation, i.e. the energy which the molecules of the reactants must have to surmount the potential barrier and transform into the products.

In the general case it is a quite complicated procedure to plot a potential energy surface, and this is done only for a small number of very simple reactions. Even this is quite approximate. If we cut the potential surface perpendicular to the plane of the drawing and along the reaction path, and unfold the surface of the cut onto one plane, the curve limiting this plane will be the profile of the reaction path shown in Fig. 5.2.

It can be seen that a reacting system before reaching its final state must surmount a potential barrier equal to $E_{cl}$, the *classical energy of activation*. The difference between the potential energies of the reactants and products is the heat of a reaction $-\Delta H$.

A more exact consideration shows that any system of atoms in no conditions whatsoever, even at the temperature of absolute zero, can have an energy less than a certain value, the so-called *zero energy*. Since the vibrational energy $\varepsilon$ of a diatomic system

$$\varepsilon = \left(n_v + \frac{1}{2}\right) h\omega \tag{5.1}$$

where $n_v$ = vibrational quantum number
$\omega$ = fundamental frequency of vibrations
$h$ = Planck constant,
then at $n_v = 0$ we have

$$\varepsilon_0 = \frac{1}{2} h\omega \tag{5.2}$$

which corresponds to the zero energy of a diatomic system having one vibrational degree of freedom. For a multiatomic system the zero energy is equal to the sum of the zero energies for all the vibrational degrees of freedom. For this reason the activation energy $E_0$ (see Fig. 5.2) corresponding to the temperature of absolute zero

is equal to

$$E_0 = E_{cl} - \left[\frac{1}{2}\sum h\omega^* - \frac{1}{2}\sum h\omega\right] N_A \qquad (5.3)$$

(summation is carried out over all the vibrational degrees of freedom of the initial state, characterized by the frequencies $\omega$, and the transition state, characterized by the frequencies $\omega^*$; $N_A$ is the Avogadro constant).

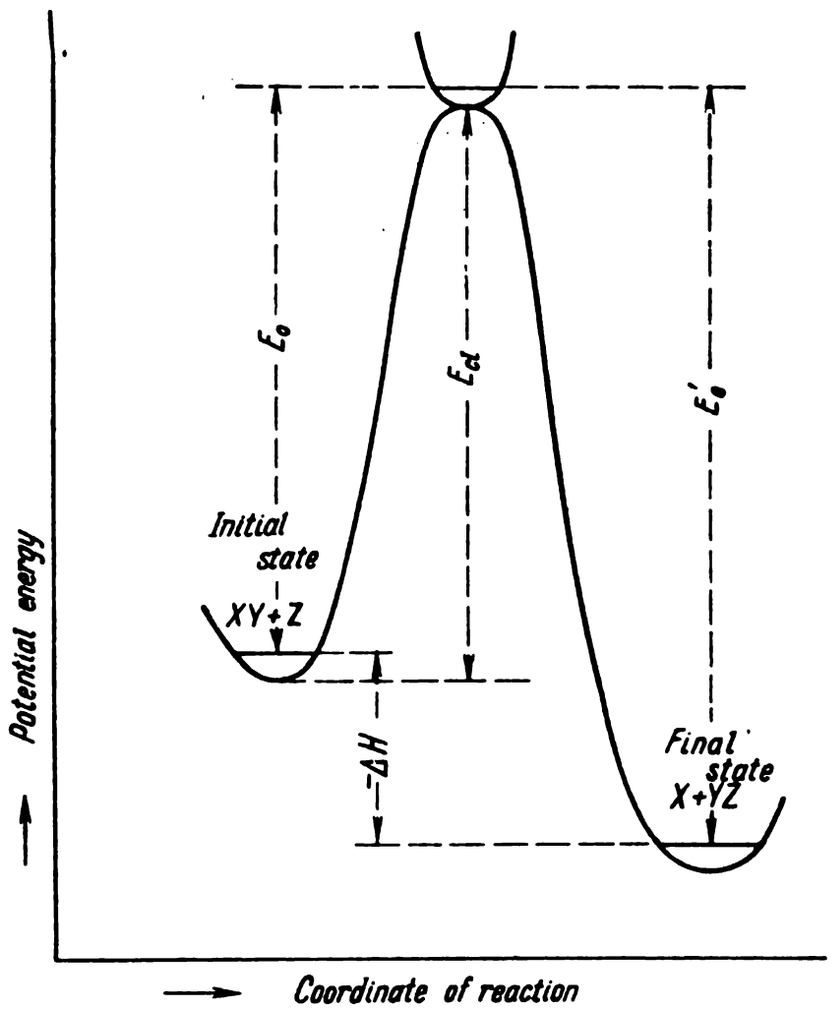



Fig. 5.2. Profile of path of reaction of type XY + Z → X + YZ

The total number of degrees of freedom which an $n$-atomic molecule has is equal to $3n$, of which three degrees of freedom (or two for a linear molecule) characterize rotation of the molecule and three determine the translational motion of the molecule as a whole. Thus the total number of vibrational degrees of freedom for a system consisting of $n$ atoms will be $3n - 6$ (for a linear system $3n - 5$). For an activated complex this number is less by unity, since one of the vibrational degrees of freedom changes into a coordinate of the reaction. Vibration of the formed complex X-Y-Z along the valence bonds leads to a reaction of decomposition. This vibration is replaced by motion of a special kind of the complex X-Y-Z leading to the formation of the molecules YZ and X. It was described above and

is depicted in Fig. 5.1 as the reaction path. This motion is considered as a form of translational motion of the activated complex. The concepts *rotation* and *vibration* when applied to an activated complex do not have their ordinary meaning, since the complex exists for a very short time. These concepts mean that the dependence of the potential and kinetic energy of the system of atoms on the coordinates and the impulses connected with them is the same as for stable molecules.

An activated complex formed from reactants can change only into the products. When atoms reach the configuration of an activated complex they continue to move by inertia in the direction of formation of the products. In reversible reactions the activated complex for the reverse reaction has the same configuration as that for the forward reaction. We cannot therefore consider the activated complex to be in equilibrium with the reactants. With the formation of an activated complex, the forward and reverse processes proceed independently.

Detailization of the theory of collisions by the introduction of a state intermediate between the initial and the final ones made it possible to use the apparatus of statistical mechanics for calculating the rates of a reaction. The method of calculating reaction rates with account of the transition state, called the *transition-state method* (M. Polanyi and M. Evans) or the *activated complex method* (H. Eyring), was developed in 1935.

**5.2. Derivation of Fundamental Equation of Activated Complex Theory.** The transition-state method is based on three assumptions. Firstly, the proceeding of a reaction does not essentially violate the distribution of the molecules by states, so that the distribution statistically corresponds to the Maxwell-Boltzmann equilibrium one. Calculations which we shall not stop to consider here show that this assumption is true in a very great number of cases. In addition, the results obtained by the transition-state method for the rates of chemical reactions agree with experiment, which indirectly also confirms this assumption.

Secondly, it is assumed that an elementary act of a reaction proceeds adiabatically. In the present case this term is only formally similar to the concept of an adiabatic process in thermodynamics and means that the nuclei of the atoms move at a much slower rate than the electrons; for this reason at each configuration of the nuclei the electrons have time to rearrange, and their motion to acquire the same nature as if the nuclei remained for an infinitely long time in one position. Thus, the adiabatic nature of motion of the nuclei leads to the fact that the latter move independently of the electrons, and the potential energy in motion of the nuclei changes continuously, since this motion is not accompanied by electron transitions

Thirdly, the motion of the nuclei in adiabatic conditions can be considered from the positions of classical mechanics. Quantum-mechanical calculations show that this assumption is strictly obeyed on the top of the potential barrier at a finite velocity of the particles. It is also obeyed near the top of the potential barrier if the particles have a sufficiently high velocity. The latter assumption appreciably simplifies the finding of the mean rate of an elementary reaction, since it allows us to use classical statistics. As we shall see below, the assumption on the adiabatic course of an elementary chemical process may also not be obeyed, but experience shows that such processes are comparatively rare.

The rate of a chemical reaction is obviously equal to the rate of passing of the activated complex over the potential barrier. Let us so select a certain finite interval $\delta$ along the coordinate of a reaction that it includes the top of the potential barrier. The configuration of atoms existing in this interval and moving in the direction of the products is the activated complex. The mean lifetime of an activated complex

$$\tau = \frac{\delta}{\bar{c}_x} \tag{5.4}$$

where $\bar{e}_x$ is the mean velocity of passage of activated complexes over the top of the potential barrier or, in other words, the mean change in the reaction coordinate with time at the top of the potential barrier (within the interval $\delta$). This quantity corresponds to the mean velocity of motion of the configuration of the atoms.

The mean velocity of activated complexes over a barrier (within the interval $\delta$) is equal to the sum of the velocities of the complexes passing over the barrier divided by the number of such complexes, i.e.

$$\bar{c}_x = \frac{\sum c_{x_i} n_i}{n} = \frac{\int_0^\infty c_x \, dn}{n} \tag{5.5}$$

According to the Maxwell-Boltzmann statistics, the number of molecules whose velocity ranges from $c_x$ to $c_x + dc_x$ is equal to

$$dn = n \sqrt{\frac{\mu}{2\pi kT}} \, e^{-\mu c_x^2/2kT} \, dc_x \tag{5.6}$$

Inserting Eq. (5.6) into Eq. (5.5), we get

$$\bar{c}_x = \frac{\int_0^\infty c_x n \sqrt{\frac{\mu}{2\pi kT}} \, e^{-\mu c_x^2/2kT} \, dc_x}{\int_{-\infty}^{+\infty} n \sqrt{\frac{\mu}{2\pi kT}} \, e^{-\mu c_x^2/2kT} \, dc_x} = \frac{\int_0^\infty c_x e^{-\mu c_x^2/2kT} \, dc_x}{\int_{-\infty}^{+\infty} e^{-\mu c_x^2/2kT} \, dc_x} \tag{5.7}$$

The integration limits in the numerator are given with account of the fact that the activated complex moves only in one direction. In the denominator all possible directions of motion are taken into consideration. Integration of Eq. (5.7) yields

$$\bar{c}_x = \left(\frac{kT}{2\pi\mu}\right)^{1/2} \tag{5.8}$$

Inserting Eq. (5.8) into Eq. (5.4), we find the mean lifetime of an activated complex:

$$\tau = \delta \left(\frac{2\pi\mu}{kT}\right)^{1/2} \tag{5.9}$$

Let us denote the concentration of the activated complexes in the interval $\delta$ on the coordinate of a reaction by $c_{ac}$. This quantity corresponds to the number of appearing activated complexes or the number of reaction acts during the time $\tau$. Hence the number of reaction acts in a unit of volume per unit of time or, in other words, the rate of a reaction, will be

$$J = \frac{c_{ac}}{\tau} = c_{ac}\left(\frac{kT}{2\pi\mu}\right)^{1/2}\frac{1}{\delta} \tag{5.10}$$

This expression is true only when the appearance of an activated complex guarantees the proceeding of the reaction, i.e. only for adiabatic processes. In a more general case Eq. (5.10) must be supplemented with an additional factor—the *transmission coefficient* $\chi \leqslant 1$. Equation (5.10) must therefore be written as follows:

$$J = \chi c_{ac}\left(\frac{kT}{2\pi\mu}\right)^{1/2}\frac{1}{\delta} \tag{5.11}$$

The elementary processes accompanied by electron transitions are non-adiabatic ones. An electron transition corresponds to the transition of the system, when it reaches the top of the barrier, from one potential surface to another. In non-adiabatic processes the reaching of the top of the potential barrier does not yet indicate an unconditional transition to the products, and there exists a finite probability of transition of the system from a lower potential surface to a higher one. Thus for non-adiabatic processes the transmission coefficient $\chi$ is less than unity. As a rule, a process proceeds non-adiabatically if the reaction is associated with a change in the total electron spin or it corresponds to some other forbidden transition. The transmission coefficient for non-adiabatic processes is most frequently of the order of $10^{-5}$. Approximate calculations show that non-adiabatic reactions are encountered quite rarely.

Let us consider the derivation of the expression for the rate constant of a chemical reaction on the example of the bimolecular reaction

$$A + B \rightarrow AB^{\star} \rightarrow \text{products}$$

where A and B = molecules of the reactants
AB* = activated complex.

Hence, according to the fundamental postulate of chemical kinetics, the rate of the reaction is

$$J = k_r c_A c_B \tag{5.12}$$

Solving the simultaneous equations (5.11) and (5.12), we get the following expression for the rate constant:

$$k_r = \chi \frac{c_{AB^*}}{c_A c_B} \left(\frac{kT}{2\pi\mu}\right)^{1/2} \frac{1}{\delta} \tag{5.13}$$

According to the first assumption (the possibility of applying the Maxwell-Boltzmann statistics to the reacting system), the rate constant of the elementary reaction A + B → C + . . ., proceeding in the absence of chemical equilibrium, differs only slightly from the rate constant of the same process calculated on the assumption of the existence of chemical equilibrium both with the products and with the intermediates that are an activated complex. For this reason Eq. (5.13) can be written as

$$k_r = \chi \frac{c_{AB^*,\,eq}}{c_{A,\,eq} c_{B,\,eq}} \left(\frac{kT}{2\pi\mu}\right)^{1/2} \frac{1}{\delta} \tag{5.14}$$

where the subscript "eq" indicates that the concentrations correspond to the state of chemical equilibrium.

The factor containing the equilibrium concentrations can be replaced by the constant of chemical equilibrium of the reactants with the configuration of the atoms corresponding to the activated complex:

$$K = \frac{c_{AB^*,\,eq}}{c_{A,\,eq} c_{B,\,eq}} \tag{5.15}$$

It is known from statistical thermodynamics that the equilibrium constant can be expressed through the statistical partition functions of the relevant substances, i.e.

$$K = \frac{Q'_{AB^*}}{Q_A Q_B} e^{-E_0/RT} \tag{5.16}$$

The energy here is counted from the zero value for the corresponding molecule or activated complex, consequently $E_0$ corresponds to the activation energy at absolute zero.

The statistical partition function of an activated complex, in contrast to that of a stable molecule, contains as a factor the degree of freedom of translational motion along the reaction path $Q_{trans}$, i.e. $Q'_{AB^*} = Q_{AB^*} Q_{trans,\,(1)}$. Statistical mechanics gives the follo-

wing expression for the statistical partition function of translational motion:

$$Q_{\text{trans}} = \frac{(2\pi\mu kT)^{3/2}}{h^3} V \tag{5.17}$$

For one degree of freedom a cubic root must be extracted from this expression, and in the given case $V^{1/3}$ will correspond to the interval $\delta$ of the reaction path being considered. Consequently, taking into account that Eq. (5.16) includes the statistical partition functions, we can write

$$Q_{\text{trans.}(1)} = (2\pi\mu kT)^{1/2} \frac{\delta}{h} \tag{5.18}$$

and

$$Q'_{AB^\star} = Q_{AB^\star} (2\pi\mu kT)^{1/2} \frac{\delta}{h} \tag{5.19}$$

Inserting Eq. (5.19) into Eq. (5.16), we get

$$K = \frac{\delta}{h} (2\pi\mu kT)^{1/2} K^\star \tag{5.20}$$

where

$$K^\star = \frac{Q_{AB^\star}}{Q_A Q_B} e^{-E_0/RT} \tag{5.21}$$

can be called the constant of equilibrium between an activated complex and the reactants. Actually, as has already been noted, such equilibrium does not exist, but we see, however, that the quantity $K^\star$ can be calculated as an ordinary equilibrium constant. Here the factor corresponding to motion along the reaction coordinate is excluded from the statistical partition function of the configuration of the atoms corresponding to the activated complex, which in such calculations may formally be considered as a simple molecule.

Let us insert Eq. (5.20) into Eq. (5.14). Hence, with an account of Eq. (5.15), we get

$$k_r = \chi \frac{kT}{h} K^\star = \chi \frac{kT}{h} \frac{Q_{AB^\star}}{Q_A Q_B} e^{-E_0/RT} \tag{5.22}$$

**5.3*. Free Activation Energy.** As is known from thermodynamics, the equilibrium constant is related to the free energy of a process. This relation can also be used for finding the value of $K^\star$, introducing the concept of *free activation energy*, that characterizes the change in the free energy when a system passes from the initial state to a transition one and takes into account all the degrees of freedom except the reaction coordinate. If the substance is in the standard state, then for a process proceeding at constant volume

$$-\Delta A^\star = RT \ln K^\star \tag{5.23}$$

Taking into account that

$$\Delta A^\star = \Delta U^\star - T\,\Delta S^\star \tag{5.24}$$

Eq. (5.23) can be written as follows:

$$K^{\star}=e^{\Delta S^{\star}/R}e^{-\Delta U^{\star}/RT} \tag{5.25}$$

Inserting this expression into Eq. (5.22), we get

$$k_{\mathrm{r}}=\chi\frac{kT}{h}e^{\Delta S^{\star}/R}e^{-\Delta U^{\star}/RT} \tag{5.26}$$

Correspondingly, if a process proceeds at constant pressure, the Gibbs energy (free energy at constant pressure) should be used. Reasoning similar to that set out above allows us to deduce an expression for the rate constant

$$k_{\mathrm{r}}=\chi\frac{kT}{h}e^{-\Delta G^{\star}/RT}=\chi\frac{kT}{h}e^{\Delta S^{\star}/R}e^{-\Delta H^{\star}/RT} \tag{5.27}$$

In these expressions for the rate constant of a chemical reaction, the quantities $\Delta U^{\star}$ and $\Delta H^{\star}$ have the physical meaning of the heats of activation, and $\Delta S^{\star}$—the entropy of activation.

Equations (5.25) and (5.26) show that a quite definite meaning can be imparted to the steric factor. As will be shown below, the quantities $\Delta U^{\star}$ and $\Delta H^{\star}$ are related to the activation energy determined experimentally, and, consequently, the factor containing the entropy of activation $\Delta S^{\star}$ corresponds to the steric factor in the theory of collisions. It follows from Eqs. (5.25) and (5.26) that the rate of a reaction is determined not by the heat of activation, but by the change in the free energy when the system passes into the transition state. If the passing into the corresponding state is accompanied by a great increase in entropy, then notwithstanding the great activation energy, the reaction will proceed at a high rate. Conversely, processes accompanied by a reduction in entropy, notwithstanding the low activation energy, will proceed slowly. Any external factor reducing the free activation energy will facilitate an increase in the rate of a chemical process. Thus the term *steric factor*, as can be seen, does not correspond to the physical meaning of this quantity, and it is therefore better to call it the *entropy factor*.

**5.4*. Experimental Value of Activation Energy.** The quantities $\Delta U^{\star}$ and $\Delta H^{\star}$ in Eqs. (5.26) and (5.27) are not experimentally determined activation energies, but the changes in the internal energy and enthalpy when the initial molecules pass over into the state of an activated complex. For practical calculations it is good to introduce the experimentally determined activation energy into these equations. If we select the pressure and temperature as independent variables, it is convenient to use Eq. (5.27) to calculate the reaction rate.

Taking logarithms of Eq. (5.22) with a variable pressure and temperature (this is indicated by the subscript $p$), we get

$$\ln k_{\mathrm{r},\,p}=\ln\chi+\ln\frac{k}{h}+\ln T+\ln K^{\star} \tag{5.28}$$

Differentiating this equation with respect to the temperature and taking into account the Arrhenius equation, we have

$$\frac{E_p}{RT^2}=\frac{d\ln k_{\mathrm{r},\,p}}{dT}=\frac{1}{T}+\frac{d\ln K_p^{\star}}{dT} \tag{5.29}$$

where $E_p$ is the experimentally found activation energy. According to the equation of the isobar of a chemical reaction

$$\frac{d\ln K_p^{\star}}{dT}=\frac{\Delta H^{\star}}{RT^2} \tag{5.30}$$

Equation (5.29) can be written in the form

$$\frac{E_p}{RT^2}=\frac{1}{T}+\frac{\Delta H^\star}{RT^2} \tag{5.31}$$

whence

$$E_p = RT + \Delta H^\star \tag{5.32}$$

Since for ideal gases the quantity $\Delta H^\star$ does not depend on the pressure, this quantity has not been related to the standard state in the equations considered above. For a selected standard state Eq. (5.27) becomes

$$k_{r,\,p}=\chi\frac{kT}{h}\,e^{-\Delta H^\star/RT}\,e^{\Delta S^\star/R} \tag{5.33}$$

Introducing the value of $\Delta H^\star$ from Eq. (5.32) into Eq. (5.33), we get

$$k_{r,\,p}=\chi e\frac{kT}{h}\,e^{-E_p/RT}\,e^{\Delta S^\star/R} \tag{5.34}$$

If the specific rate is expressed in units of volume concentration, then taking into account that

$$K_p^\star=K_c^\star\,(RT)^{x-1} \tag{5.35}$$

(where $x$ is the number of molecules entering the activated complex), the expression for the specific rate of a reaction, as follows from Eq. (5.22), will be

$$k_r=k_{r,\,p}\,(RT)^{x-1} \tag{5.36}$$

For a process proceeding at constant volume, we get [see Eq. (5.29)]

$$\frac{E_{\exp}}{RT^2}=\frac{d\ln K_c}{dT}=\frac{1}{T}+\frac{d\ln K_c^\star}{dT} \tag{5.37}$$

whence

$$E_{\exp} = RT + \Delta U^\star = RT + \Delta H^\star - p\Delta V^\star \tag{5.38}$$

where $\Delta V^\star$ is the change in volume upon transition to the activated state.

For a reaction proceeding in a gaseous phase, on condition that the gas is ideal, we have

$$p\Delta V^\star = (1 - x)\,RT \tag{5.39}$$

Inserting this equation into Eq. (5.38) and taking into account Eq. (5.32), we get

$$E_{\exp} = E_p + (x - 1)\,RT \tag{5.40}$$

Inserting Eqs. (5.36) and (5.40) into Eq. (5.34), we have

$$k_r=\chi e\frac{kT}{h}\,e^{-E_{\exp}/RT}\,e^{\Delta S_p^\star/R}\,(RT)^{x-1} \tag{5.41}$$

For solutions the standard state corresponds to a concentration (or activity) equal to unity, and therefore Eq. (5.27) should be written as follows:

$$k_r=\chi\frac{kT}{h}\,e^{\Delta S_c^\star/R}\,e^{-\Delta H^\star/RT} \tag{5.42}$$

where $\Delta H^\star$ is written without indicating the standard state, since the system is considered to be ideal. Owing to the fact that for solutions $\Delta V^\star$ is practically equal to zero, Eq. (5.41) becomes

$$k_{r,\,sol}=\chi e\frac{kT}{h}\,e^{-E_{\exp}/RT}\,e^{\Delta S_c^\star/R} \tag{5.43}$$

**5.5. Interaction of Two Atoms. Comparison of Collision and Activated Complex Theories.** Let us consider the calculation of the rate of the reaction between two atoms by the activated complex method. Let $m_A$ and $m_B$ be the masses of the atoms, and $r_A$ and $r_B$ their effective radii. Here the activated complex will be similar to a diatomic molecule of the type AB. The partition functions for atoms having only three translational degrees of freedom are

$$Q_A = \frac{(2\pi m_A kT)^{3/2}}{h^3} \quad \text{and} \quad Q_B = \frac{(2\pi m_B kT)^{3/2}}{h^3} \tag{5.44}$$

An activated complex formally has four translational degrees of freedom (account of one of which, corresponding to the movement of the complex along the coordinate of the reaction, led to the appearance of the factor $kT/h$) and two rotational degrees of freedom. The partition function of the activated complex is

$$Q_{AB^*} = Q_{AB^*(\text{trans})} Q_{AB^*(\text{rot})} = \frac{[2\pi (m_A + m_B) kT]^{3/2}}{h^3} \frac{8\pi^2 IkT}{h^2} \tag{5.45}$$

where $I$ is the moment of inertia of the activated complex;

$$I = \frac{m_A m_B}{m_A + m_B} (r_A + r_B)^2 \tag{5.46}$$

here $r_A + r_B$ is the effective radius of the activated complex.

Inserting Eq. (5.46) into Eq. (5.45), we get

$$Q_{AB^*} = \frac{[2\pi (m_A + m_B) kT]^{3/2}}{h^3} \frac{8\pi^2 m_A m_B kT}{h^2 (m_A + m_B)} (r_A + r_B)^2 \tag{5.47}$$

Knowing the partition functions, we can compute the rate constant of a reaction. Assume that $\chi = 1$ and $E_0 = 0$. Inserting into Eq. (5.22) the values of the partition functions from Eqs. (5.44) and (5.47), we get the number of molecules colliding (reacting) in a unit of volume per unit of time:

$$k_r = (r_A + r_B)^2 \left(8\pi kT \frac{m_A + m_B}{m_A m_B}\right)^{1/2} \tag{5.48}$$

According to the collision theory, the number of colliding molecules in a unit of volume per unit of time on condition that $n_A = n_B = 1$ is

$$Z = \pi \sigma_{1,2}^2 \bar{c} \tag{5.49}$$

Inserting into this expression the value of $\bar{c}$ from Eq. (3.52) and taking into consideration that $\sigma_{1,2} = r_A + r_B$, we get

$$Z = (r_A + r_B)^2 \left(8\pi^2 kT \frac{m_A + m_B}{m_A m_B}\right)^{1/2} \tag{5.50}$$

which coincides with the value given by the activated complex theory [Eq. (5.48)]. Thus the collision and activated complex theories give identical results for the interaction of two atoms.

Let us see whether the results of calculating the reaction rates by the collision method will coincide with those calculated by the activated complex method if molecules and not atoms react. For this purpose let us simplify the problem and consider that for each kind of energy of a complex molecule the partition function consists of the same factors, one per degree of freedom. Denoting the translational, rotational and vibrational partition functions per degree of freedom by $Q_{\text{trans}}$, $Q_{\text{rot}}$ and $Q_{\text{vib}}$, we can express the summary partition function as

$$Q = Q^t_{\text{trans}} Q^r_{\text{rot}} Q^v_{\text{vib}} \tag{5.51}$$

where $t$, $r$ and $v$ are the corresponding numbers of degrees of freedom.

For the reaction between atoms discussed above the partition functions of particles in equilibrium are equal to

$$Q_A = Q^3_{\text{trans}}; \quad Q_B = Q^3_{\text{trans}}; \quad Q_{AB^\star} = Q^3_{\text{trans}} Q^2_{\text{rot}} \tag{5.52}$$

and the preexponential term in Eq. (5.22) for the rate constant of the reaction will be

$$\frac{kT}{h} \frac{Q_{AB^\star}}{Q_A Q_B} = \frac{kT}{h} \frac{Q^2_{\text{rot}}}{Q^3_{\text{trans}}} \tag{5.53}$$

But, as indicated above, this expression is the number of collisions of atoms A with atoms B in a unit of volume per unit of time on condition that $n_A = n_B = 1$, i.e.

$$Z = \frac{kT}{h} \frac{Q^2_{\text{rot}}}{Q^3_{\text{trans}}} \tag{5.54}$$

For non-linear polyatomic molecules A and B consisting of $n_A$ and $n_B$ atoms, the partition functions can be written as follows:

$$\left.\begin{aligned} Q_A &= Q^3_{\text{trans}} Q^3_{\text{rot}} Q^{3n_A-6}_{\text{vib}} \\ \text{and} \quad Q_B &= Q^3_{\text{trans}} Q^3_{\text{rot}} Q^{3n_B-6}_{\text{vib}} \end{aligned}\right\} \tag{5.55}$$

and for an activated complex having one vibrational degree of freedom less than a molecule consisting of the same number of atoms

$$Q_{AB^\star} = Q^3_{\text{trans}} Q^3_{\text{rot}} Q^{3(n_A+n_B)-7}_{\text{vib}} \tag{5.56}$$

Hence the preexponential factor in Eq. (5.22) will be equal to

$$\frac{kT}{h} \frac{Q_{AB^\star}}{Q_A Q_B} = \frac{kT}{h} \frac{Q^5_{\text{vib}}}{Q^3_{\text{trans}} Q^3_{\text{rot}}} \tag{5.57}$$

or, with account of Eq. (5.54)

$$\frac{kT}{h} \frac{Q_{AB^\star}}{Q_A Q_B} = Z \left( \frac{Q_{\text{vib}}}{Q_{\text{rot}}} \right)^5 \tag{5.58}$$

In the general case of interaction of two non-linear polyatomic molecules (for initial molecules of other types somewhat different expressions are obtained) the activated complex theory gives a value for the rate differing from that given by the collision theory [see Eq. (5.50)] by the factor $(Q_{vib}/Q_{rot})^5$, therefore the so-called steric factor introduced previously, on the basis of the activated complex theory, is equal to

$$P \approx \left(\frac{Q_{vib}}{Q_{rot}}\right)^5 \tag{5.59}$$

Since the partition function for the vibrational energy is close to unity, and the rotational partition function ranges from 10 to $10^2$, the extreme values of the steric factor according to the above approximate relation may reach values from $10^{-5}$ to $10^{-10}$. This factor, since it is associated with the entropy, is sometimes called the *probability factor*.

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As can be seen from what has been considered above, if the configuration of the reacting molecules and the activated complex is known, the activated complex method makes it possible to calculate the preexponential factor. But in the majority of cases the structure of the activated complex and its properties are not known, and this hinders calculations. As regards the calculation of the activation energy of a chemical reaction, this is the task of quantum chemistry. Meanwhile the methods of solving this problem do not make it possible to obtain quantitative results. Notwithstanding the drawbacks indicated, however, the activated complex method makes it possible to obtain qualitative results which help us to understand the laws of how chemical processes proceed.

# CHAPTER 6

# MONOMOLECULAR AND TRIMOLECULAR REACTIONS

**6.1. Monomolecular Reactions. Experimental Data and Tasks of Theory.** The main features making it possible to experimentally determine a monomolecular reaction in a gaseous phase are as follows.

1. The kinetics of the reaction satisfies a first-order equation, and thus the rate constant does not depend on the concentration (pressure).

2. The reaction is strictly homogeneous, and the walls of the vessel do not influence its course.

The thermal decomposition of a number of chemical compounds complies with these conditions.

TABLE 6.1

**Kinetics of Thermal Decomposition of Oxygen Compounds of Nitrogen and the Halogens**

| Molecule | Temperature interval, K | Pressure interval, mm Hg | Rate constant, $s^{-1}$ |
|---|---|---|---|
| $N_2O$ | 833-1273 | 8.1-8000 | $3\times10^{9}e^{-52\,000/RT}$ |
| $N_2O_5$ | 273-338 | $2\times10^{-4}$-70 | $4.5\times10^{13}e^{-24\,500/RT}$ |
| $Cl_2O_7$ | 373-393 | 1.5-80 | $4.5\times10^{15}e^{-32\,900/RT}$ |
| $NO_2Cl$ | 453-523 | 3-9 | $5.8\times10^{16}e^{-27\,500/RT}$ |
| $NO_3Cl$ | 363-403 | 8-200 | $1.5\times10^{14}e^{-30\,000/RT}$ |
| $FClO_2$ | 593-653 | 6-500 | $1.5\times10^{13}e^{-44\,800/RT}$ |
| $FClO_3$ | 738-768 | 5-930 | $3.9\times10^{13}e^{-58\,400/RT}$ |

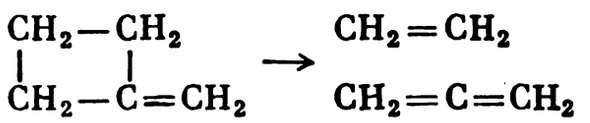
1. *Decomposition of Oxygen Compounds of Nitrogen and the Halogens.* Table 6.1 gives kinetic data on the decomposition of oxygen compounds of nitrogen and the halogens. The high values of the activation energy and the preexponential factor (the latter for all the compounds except $N_2O$) attract attention.

The first monomolecular reaction to be discovered was the reaction of decomposition of nitrogen pentoxide, which apparently proceeds as follows:

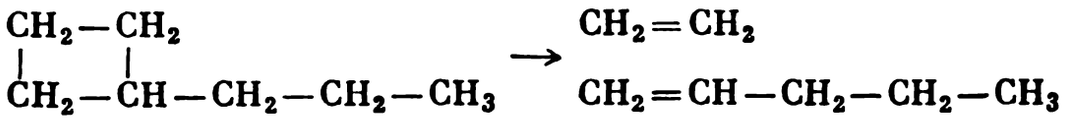
$$N_2O_5 \rightarrow N_2O_3 + O_2$$
$$N_2O_3 + N_2O_5 \rightarrow 4NO_2$$

the rate being determined by the first step. The studying of this reaction played a great role in the development of theoretical notions. The matter is that the rate constant in the investigated range of pressures (from 0.0002 to 70 mm Hg) was found to be independent of the pressure only to 0.6 mm Hg, and at lower pressures its value systematically decreases. Later a critical pressure below which the reaction stops obeying the kinetic law of a first-order reaction and the rate constant begins to depend on the pressure in the same way as the rate constant of a second-order reaction was also discovered for many other monomolecular reactions. The explanation of this, at a first glance, paradox was one of the tasks of the theory of kinetics.

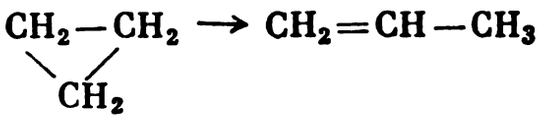
2. *Pyrolysis of Hydrocarbons.* The mechanism of the thermal decomposition of hydrocarbons in the course of which a relatively high concentration of radicals is quite probable, is as a rule a chain one. The processes of decyclization of certain cycloparaffins were also found to be monomolecular ones. Examples are the decomposition of methylene cyclobutane into allene and ethylene



proceeding like a first-order reaction ($k_r = 4.76 \times 10^{15} \times \times e^{-63\,300/RT}\ s^{-1}$) to a pressure of 2 mm Hg and changing into a second-order reaction at higher pressures; the decyclization of propyl cyclobutane



($k_r = 3.4 \times 10^{15} e^{-61\,600/RT}\ s^{-1}$); and the isomerization of cyclopropane



($k_r = 1.98 \times 10^{15} e^{-65\,100/RT}\ s^{-1}$).

3. *Decomposition of Aliphatic Halogen Derivatives.* The thermal decomposition of alkyl halides leads to the formation of hydrogen halide and the corresponding olefin, for example,

$$CH_3-CHCl-CH_3 \rightarrow CH_3-CH=CH_2 + HCl$$

TABLE 6.2

**Kinetics of Thermal Decomposition of Hydrocarbon Halogen Derivatives**

| Molecule | Temperature interval, K | Pressure interval, mm Hg | Transition pressure, mm Hg | Rate constant, $s^{-1}$ |
|---|---|---|---|---|
| $C_2H_5Cl$ | 723-773 | 0.5-220 | 8 | $3.9\times10^{14}e^{-60\,800/RT}$ |
| $CH_3CHCl_2$ | 641-723 | 0.5-410 | 20 | $4.5\times10^{11}e^{-48\,300/RT}$ |
| $CH_3CHClCH_3$ | 673-683 | 0.1-440 | 4 | $10^{14}e^{-50\,600/RT}$ |
| $CH_3CCl_2CH_3$ | 603-690 | 8-50 | — | $7.9\times10^{11}e^{-43\,900/RT}$ |
| $CH_3CH_2CHCl_2$ | 603-700 | 17-61 | — | $5.8\times10^{12}e^{-51\,200/RT}$ |
| $CH_3CHClCH_2CH_3$ | 603-663 | — | — | $4.1\times10^{13}e^{-49\,500/RT}$ |
| $CH_3CH_2CH_2CH_2Cl$ | 664-731 | 80-200 | — | $10^{14}e^{-57\,000/RT}$ |
| $C_2H_5Br$ | 583-749 | 80-300 | — | $3.8\times10^{12}e^{-46\,400/RT}$ |
| $CH_2=CHCH_2Br$ | 320-380 | — | 300 | $2.1\times10^{12}e^{-45\,400/RT}$ |

Decomposition of a compound with two halogen atoms at a carbon atom leads to the formation of an acetylene derivative:

$$CH_3-CCl_2-CH_3 \rightarrow CH_3-C\equiv CH+2HCl$$

Table 6.2 gives kinetic data on the monomolecular decomposition of halogen derivatives of hydrocarbons. The activation energy varies from 43 000 to 60 000 cal/mol.

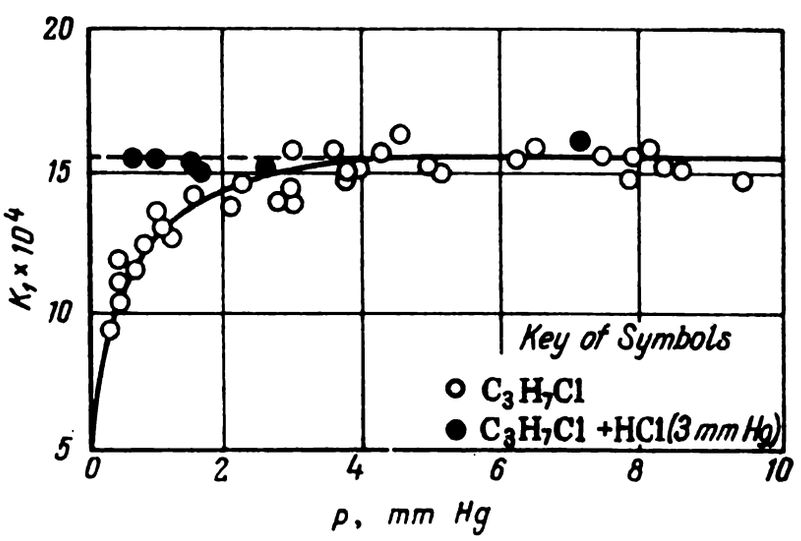



Fig. 6.1. Dependence of rate constant of monomolecular reaction on pressure (decomposition of isopropyl chloride)

Figure 6.1 shows how the rate constant depends on the pressure for the reaction of decomposition of isopropyl chloride. The rate constant at pressures exceeding 4 mm Hg (the pressure at which

a first-order reaction changes into a second-order one—the *transition pressure*) remains constant, and at pressures below the transition one it diminishes. The addition of hydrogen chloride at pressures greater than the transition one regardless of the concentration of the addition does not affect the rate constant, as matters should be on the basis of formal kinetic considerations. The picture changes when we pass over to pressures below the transition one. Here the addition of hydrogen chloride returns the rate constant to its initial value corresponding to a monomolecular process. This fact is typical and can be explained theoretically.

4. *Decomposition of Organic Oxygen Compounds.* Table 6.3 gives kinetic data on the decomposition of ethers and esters proceeding as a monomolecular reaction.

TABLE 6.3

**Kinetics of Thermal Decomposition of Ethers and Esters**

| Molecule | Temperature interval, K | Pressure interval, mm Hg | Transition pressure, mm Hg | Rate constant, $s^{-1}$ |
|---|---|---|---|---|
| $CH_3OCH_3$ | 695-825 | 3-400 | 350 | $1.9\times10^{13}e^{-57\,200/RT}$ |
| $CH_3OC_2H_5$ | 659-733 | 2.6-54 | — | $1.2\times10^{12}e^{-46\,000/RT}$ |
| $CH_3OC_3H_7$ | 673-723 | 22-336 | 100 | $8.4\times10^{12}e^{-49\,000/RT}$ |
| $C_2H_5OC_2H_5$ | 699-861 | 2.5-200 | 150 | $3.1\times10^{11}e^{-51\,800/RT}$ |
| $CH_3COOC_2H_5$ | 778-875 | 15-20 | — | $3.9\times10^{12}e^{-48\,000/RT}$ |
| $C_2H_5COOC_2H_5$ | 778-875 | 15-20 | — | $5.2\times10^{12}e^{-48\,500/RT}$ |
| $CHOOC(CH_3)_3$ | 503-573 | — | — | $1.3\times10^{11}e^{-34\,600/RT}$ |

The decomposition of certain other organic oxygen compounds also complies with the conditions of proceeding of monomolecular reactions. These include the decomposition of ethyl alcohol ($k_r = 10^{10}e^{-46\,200/RT}$ $s^{-1}$), propyl alcohol ($k_r = 7.9 \times 10^{10}e^{-49\,950/RT}$ $s^{-1}$) and isopropyl alcohol ($k_r = 2.5 \times 10^{8}e^{-34\,000/RT}$ $s^{-1}$) at temperatures exceeding 800 K, the decomposition of trioxane $(CH_2O)_3$ ($k_r = 5.3 \times 10^{12}e^{-48\,500/RT}$ $s^{-1}$), and also the decomposition of ethylene oxide ($k_r = 8.4 \times 10^{12}e^{-50\,900/RT}$ $s^{-1}$) proceeding at 651-788 K and changing into a second-order reaction at 285 mm Hg. Complications of theoretical interest are also encountered, however. For example, in the decomposition of acetic aldehyde

$$CH_3CHO \longrightarrow CHO\cdot + CH_3^{\cdot}$$

the radicals $CH_3^{\cdot}$ and $CHO\cdot$ are obtained. At sufficiently high temperatures they rapidly recombine and have no appreciable influence on the proceeding process. But at low pressures their lifetime grows

and the possibility of the development of chain processes appears. In practice this is expressed in that with a reduction of the pressure to below a definite limit, the rate constant begins to grow. The chain process can be suppressed by adding gases that interact with the radicals. The action of nitric oxide NO whose molecule contains one unpaired electron is especially characteristic. Upon colliding with

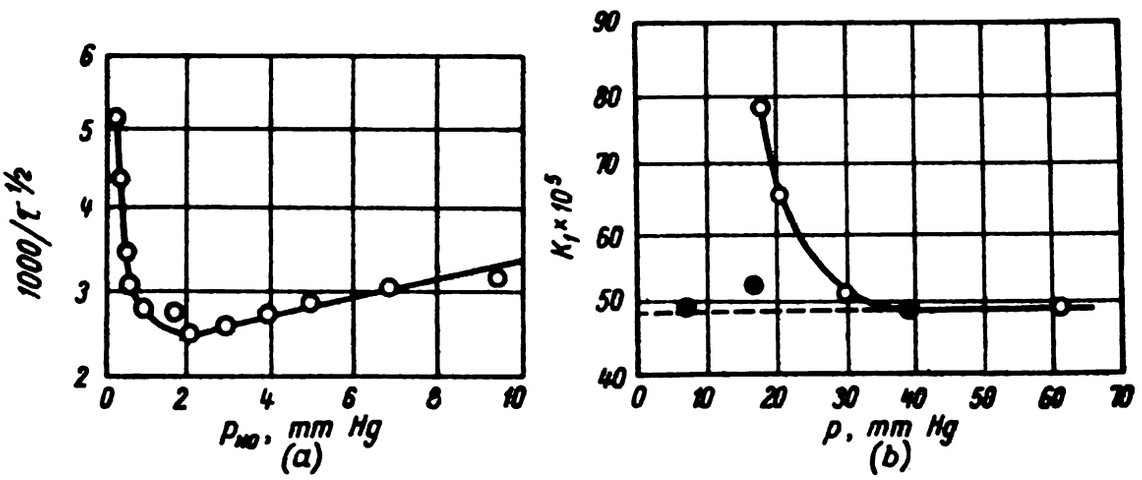



Fig. 6.2. Influence of additions on rate constant of monomolecular reaction: *a*—decomposition of $CH_3CHO$; *b*—decomposition of 1,1-dichloropropane. The white circles show $CH_3CH_2CHCl_2$, the black circles show $CH_3CH_2CHCl_2$ + iso-$C_4H_8$ (10 mm Hg); $k_1$ is the rate constant of a first-order reaction

a free radical, a molecule of NO easily combines with it, interrupting the chain. For this reason the rate constant changes with an increase in the pressure of the NO added (Fig. 6.2*a*) and comes into agreement with the value characteristic of the given monomolecular reaction.

A similar phenomenon is observed in the decomposition of propionic aldehyde and many other compounds. For example, the addition of isobutylene has a similar action on the decomposition of 1,1-dichloropropane (see Fig. 6.2*b*).

5. *Decomposition of Organic Nitrogen-Containing Compounds.* Table 6.4 gives kinetic data on the thermal decomposition of azo compounds having the following mechanism:

$$CH_3-N=N-C_3H_7 \longrightarrow N_2+CH_3^{\bullet}+C_3H_7^{\bullet}$$

The two radicals formed upon the decomposition of the same molecule recombine with a high probability simultaneously with the elementary act of decomposition

$$CH_3^{\bullet}+C_3H_7^{\bullet} \longrightarrow C_4H_{10}$$

Owing to this fact, the reaction is not complicated by chain processes even at the lowest pressures investigated (down to $10^{-2}$ mm Hg), and the addition of gases (CO, NO, etc.) trapping free radicals does not affect the course of the process.

TABLE 6.4

**Kinetics of Thermal Decomposition of Azo Compounds**

| Molecule | Temperature interval, K | Pressure interval, mm Hg | Transition pressure, mm Hg | Rate constant, $s^{-1}$ |
|---|---|---|---|---|
| $CH_3N=NCH_3$ | 551-603 | 0.026-70 | 40 | $1.1\times10^{16}e^{-50\,000/RT}$ |
| $CH_3N=NC_3H_7$ | 523-605 | 0.0058-130 | 25 | $2.8\times10^{15}e^{-46\,000/RT}$ |
| $C_3H_7N=NC_3H_7$ | 523-563 | 0.025-5 | 0.25 | $5.6\times10^{13}e^{-40\,000/RT}$ |
| $(CH_3)_3CN=NC(CH_3)_3$ | 453-493 | — | — | $2.2\times10^{16}e^{-42\,800/RT}$ |

In addition to azo compounds, monomolecular decomposition is also characteristic of amines, for example ethyl amine ($k_r = 2.9\times10^{9}e^{-42\,500/RT}$ $s^{-1}$), secondary propyl amine $k_r = 6.1\times10^{14}e^{-67\,100/RT}$ $s^{-1}$) and dimethylnitramine [$CH_3N(NO_2)CH_3$], and also of dimethyl hydrazine [$H_2N-N(CH_3)_2$], acetaldoxime ($CH_3CH=NOH$), and aliphatic nitro compounds. Kinetic data on these reactions are given in Table 6.5.

TABLE 6.5

**Kinetics of Thermal Decomposition of Nitro Compounds**

| Molecule | Temperature interval, K | Rate constant, $s^{-1}$ |
|---|---|---|
| $CH_3NO_2$ | 693-753 | $2.7\times10^{13}e^{-50\,000/RT}$ |
| $C_2H_5NO_2$ | 593-713 | $6.8\times10^{10}e^{-39\,700/RT}$ |
| | 733 | $3.6\times10^{17}e^{-60\,600/RT}$ |
| $(CH_3)_2CHNO_2$ | 523-610 | $1.1\times10^{11}e^{-39\,300/RT}$ |
| $(CH_3)_2C(NO_2)_2$ | 447-483 | $3.2\times10^{18}e^{-50\,500/RT}$ |

An interesting phenomenon was discovered in the decomposition of nitroethane. At temperatures exceeding 730 K the activation energy grows 1.5 times and the preexponential factor grows $10^7$ times. A change in the reaction mechanism corresponds to this fact. Beginning from 730 K the reaction proceeds with breaking of the C—N bond. A similar fact was discovered recently in studying the pyrolysis of hexafluoroacetone. The following reaction proceeds within the temperature interval 823 to 843 K:

$$CF_3COCF_3 \longrightarrow C_2F_6 + CO$$

($k_r = 4 \times 10^9 e^{-50\,900/RT}$ $s^{-1}$). The direction of the process changes with an increase in the temperature (843 to 923 K) and the following reaction proceeds:

$$CF_3COCF_3 \longrightarrow CF_3COF + \frac{1}{2} C_2F_4$$

The value of the rate constant changes accordingly ($k_r = 4 \times \times 10^{16} e^{-79\,100/RT}$ $s^{-1}$). The last two examples illustrate a sufficiently general law in chemical kinetics established experimentally, namely, a process with a higher activation energy prevails with an increase in the temperature.

6. *Decomposition of Tetraalkyls of Elements of Group IV.* Kinetic data on these reactions are given in Table 6.6. Exceedingly great activation energies and high values of the preexponential factors are especially characteristic of the decomposition of tetraalkyls proceeding according to the reaction

$$Si(CH_3)_4 \longrightarrow Si + 4CH_3^{\cdot}$$

The free radicals formed as a result of the elementary acts rapidly recombine and, in the same way as in the decomposition of azo compounds, the chain mechanisms are not significant, and the addition of NO and CO does not affect the course of the process.

TABLE 6.6

**Kinetics of Thermal Decomposition of Tetraalkyls of Elements of Group IV**

| Molecule | Temperature interval, K | Pressure interval, mm Hg | Transition pressure, mm Hg | Rate constant, $s^{-1}$ |
|---|---|---|---|---|
| $Si(CH_3)_4$ | 733-933 | 4.4-584 | 10 | $1.6 \times 10^{15} e^{-78\,000/RT}$ |
| $Ge(C_2H_5)_4$ | 692-715 | 1.7-465 | 8 | $1.9 \times 10^{14} e^{-51\,000/RT}$ |
| $Sn(CH_3)_4$ | 713-766 | 0.1-170 | 80 | $8.1 \times 10^{21} e^{-82\,000/RT}$ |

From a brief consideration of the main facts discovered experimentally in studying monomolecular reactions, it follows first of all that a monomolecular mechanism is much more widespread than a bimolecular one, if we limit ourselves to consideration of the kinetic properties of valence-saturated molecules. It is quite obvious that molecules having a sufficiently complicated structure undergo, as a rule, monomolecular transformation. It should be noted that the activation energy and the preexponential factors are quite great in comparison with the relevant quantities for other classes of chemical processes. The observed exclusions, for example the decomposition of $N_2O$, do not change the general picture.

**6.2. Bimolecular Mechanism of Activation of Monomolecular Reaction.** The existence of monomolecular reactions and the features of their proceeding confront the theory of chemical kinetics with a number of important problems:

1. What is the mechanism of activation of molecules in a monomolecular transformation?

The process of activation by collision is mainly a bimolecular one, and it should seem that the rate of any reaction activated as a result of a collision should be directly proportional to the square of the pressure (or concentration). The rate of a monomolecular reaction, however, is proportional to the first power of the pressure (or concentration). Consequently, in monomolecular transformations activation is accomplished not as a result of collisions, but as a result of some other process. For this reason the first attempts to explain monomolecular reactions theoretically consisted in searches for an activation mechanism (without account of molecular collisions in the reacting system). The assumption was made, for example, that activation occurs as a result of absorption of infrared radiation, i.e. is a photochemical process (R. Perrine). The opinion existed that the energy essential for activation is transmitted by the excited products and that the existence of monomolecular reactions is explained by the presence of energy circuits in the system (J. Christiansen and H. Kramers). Experiments did not confirm these assumptions, and the serious idea was even proposed that in monomolecular reactions the first law of thermodynamics is not obeyed (W. Thomson).

2. What is the reason for the change of first-order kinetics to second-order kinetics at low pressures?
3. What is the mechanism of action of the additions that return a reaction to a monomolecular one at low pressures?
4. How can the exceedingly great values of the preexponential factors [up to $10^{21}$] for certain reactions be explained?

In 1922 F. Lindemann proposed a scheme making it possible to understand the mechanism of monomolecular reactions on the basis of notions on the collision of molecules. For a monomolecular decomposition of molecule A to occur, it is essential that it have a vibrational energy sufficient for breaking of the bonds. The molecule can accumulate this energy as a result of collisions, i.e. the process of activation of a molecule can be written in the form

$$A + A \xrightarrow{k_1} A^* + A$$

where $A^*$ is an excited molecule.

Deactivation also occurs as a result of collisions, simultaneously with the process of activation:

$$A^* + A \xrightarrow{k_2} A + A$$

As a result of these processes the concentration of the active molecules $[A^*]$ is kept constant, according to the Maxwell-Boltzmann distribution. When a reaction does not proceed, the fraction of the active molecules does not depend on the pressure (concentration), and their number is directly proportional to the pressure (concentration),

since a change in the pressure leads to a proportional change in the rates of activation and deactivation. When a chemical reaction proceeds, the concentration of the active particles will also diminish as a result of their decomposition:

$$A^{\star} \xrightarrow{k_3} \text{Products}$$

In a steady-state process the constancy of the concentration of the active molecules will be determined by the condition:

rate of activation = rate of deactivation + rate of reaction, i.e.

$$k_1 [A]^2 = k_2 [A][A^{\star}] + k_3 [A^{\star}] \tag{6.1}$$

whence

$$[A^{\star}] = \frac{k_1 [A]^2}{k_2 [A] + k_3} \tag{6.2}$$

and the rate of the reaction

$$-\frac{d[A]}{dt} = k_3 [A^{\star}] = \frac{k_1 k_3 [A]^2}{k_2 [A] + k_3} \tag{6.3}$$

The active molecules $A^{\star}$ have a definite mean lifetime $\tau_{A^{\star}}$ depending on the probability of transformation of $A^{\star}$ into the products. Taking into account the relation between $\tau_{A^{\star}}$ and the time between collisions $\tau_{col}$, Eq. (6.3) can be written in two limiting forms. At high pressures the collisions are so frequent ($\tau_{col} \ll \tau_{A^{\star}}$) that almost all the molecules $A^{\star}$ become deactivated without having time to react, i.e.

$$k_2[A] \gg k_3$$

and

$$-\frac{d[A]}{dt} = \frac{k_1 k_3}{k_2} [A] = k_{\infty} [A] \tag{6.4}$$

Thus, kinetically this process is a first-order reaction.

With a reduction of the pressure, the time between collisions grows and may exceed the lifetime of an active molecule ($\tau_{col} \gg \tau_{A^{\star}}$). Here the majority of the molecules, having no time to become deactivated, will undergo transformation, i.e.

$$k_3 \gg k_2 [A]$$

and

$$-\frac{dA}{dt} = k_1 [A]^2 \tag{6.5}$$

Kinetically this corresponds to a second-order reaction.

Thus Lindemann's theoretical scheme gives the following replies to the questions confronting the theory of monomolecular reactions:

1. For monomolecular reactions activation is also the result of collisions, i.e. is a bimolecular process. With the increasing complexity of the structure of a molecule, the lifetime of an activated complex grows as a result of redistribution of the energy of collision among the internal degrees of freedom of a molecule. Owing to this

fact the rate of a reaction is found to be proportional not to the number of collisions, but to the fraction of the active molecules in the reacting system. This fraction, in turn, is directly proportional to the total number of reacting molecules. Hence follows the observance of a kinetic law of the first order.

2. According to Lindemann's scheme, there is no difference of principle between a monomolecular and a bimolecular reaction mechanism. The entire difference between them consists in the relation between the lifetime of an activated complex and the interval of time between collisions. For diatomic and triatomic molecules (for example $I_2$, NOCl, $NO_2$) in which all the energy received upon a collision is concentrated on one or two bonds, the lifetime of an activated complex is short and decomposition occurs before a molecule has time to become deactivated as a result of a collision. For this reason all the molecules activated by collisions react, and a kinetic equation of the second order is observed. Here also, at least theoretically, a transition to the kinetics of a first-order reaction is possible upon a sharp increase in the pressure. For complex molecules the transition to second-order kinetics is found to be possible only when the time between collisions grows to values that are considerably greater than the lifetime of an activated complex (see Sec. 3.9). This occurs when the pressure is decreased to a value characteristic of each given molecular system.

Lindemann's scheme not only makes it possible to explain the change of first-order kinetics into second-order kinetics with a change in the pressure, but also gives an analytical relation between the rate constant and the pressure. The rate of a monomolecular reaction determined from experiments is equal to

$$-\frac{d[A]}{dt} = k[A] \tag{6.6}$$

where $k$ is the rate constant of a reaction found experimentally. Comparing Eqs. (6.6) and (6.3), we get

$$k = \frac{k_1 k_3 [A]}{k_2 [A] + k_3} \tag{6.7}$$

or

$$\frac{1}{k} = \frac{k_2}{k_1 k_3} + \frac{1}{k_1 [A]} \tag{6.8}$$

Inserting into Eq. (6.8) the expression $[A] = p_A/RT$ and introducing the notation $k_2/k_1k_3 = 1/k_\infty$, we get an experimental dependence of the rate constant on the pressure, namely,

$$\frac{1}{k} = \frac{1}{k_\infty} + \frac{\text{const}}{p_A} \tag{6.9}$$

According to Eq. (6.9), in the coordinates $1/k$ versus $1/p_A$ we should get a linear relation that allows us to calculate the limiting value of the constant $k_\infty$ at great (formally at $p \to \infty$) pressures.

In some cases, for example in the decomposition of dimethyl ether at 777 K ($1/k = 1170 + 1.66 \times 10^{-5}\ 1/p$ and $k_\infty = 8.56 \times 10^{-4}\ s^{-1}$) this law is obeyed quite well (Fig. 6.3*a*). In others, for example in the decomposition of nitrile chloride at 413 K ($1/k = 500 + 1.59 \times \times 10^{-5}\ 1/p$ and $k_\infty = 2 \times 10^{-3}\ s^{-1}$) deviations are observed from it (Fig. 6.3*b*).

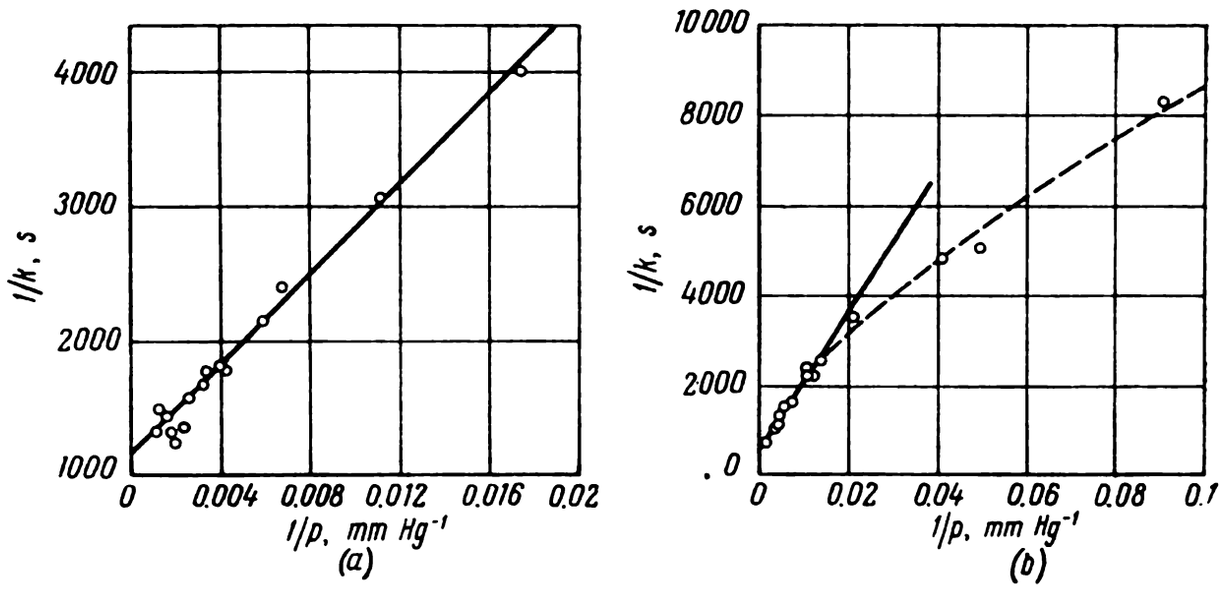



Fig. 6.3. Pressure dependence of rate constant of a monomolecular reaction: *a*—decomposition of dimethyl ether; *b*—decomposition of nitrile chloride

3. Lindemann's scheme explains the action of additions returning a reaction to a monomolecular one by the fact that the molecules of the added substance upon colliding with excited molecules of a reacting substance deactivate the latter, returning them to their initial unreactive state, while upon colliding with unexcited molecules they activate them, on the contrary. It is of interest that the molecules of added gases increase the rate of a monomolecular reaction to a value characteristic of a high pressure, but do not make it possible to exceed this value. Consequently, their role is not specific and consists only in maintaining an equilibrium concentration of the active molecules of the reacting substance according to the Maxwell-Boltzmann distribution. The part played by a molecule in the transfer of energy in monomolecular decomposition depends on its chemical nature and in general grows with an increase in the molecular mass and the number of atoms in a molecule. Below is given the relative effectiveness of the action of additions of various gases on the monomolecular reaction[1]

$$NO_2Cl \longrightarrow NO_2 + \frac{1}{2}\ Cl_2$$

[1] The decomposition of NOCl is a bimolecular reaction, while the decomposition of $NO_2Cl$ and moreover $NO_3Cl$ a monomolecular one. These reactions are an excellent illustration of the dependence of the monomolecular mechanism on the complexity of the structure of a molecule.

at 3-9 mm Hg, i.e. in conditions in which the process obeys the equation of a second-order reaction

| Gas . . . . . | He | Ne | $O_2$ | Xe | $CO_2$ | $SiF_4$ | HCl | $CCl_2F_2$ | $NO_2$ |
|---|---|---|---|---|---|---|---|---|---|
| Relative effectiveness of energy transfer . . . | 1 | 2.2 | 2.3 | 3.0 | 3.2 | 3.4 | 4.1 | 4.7 | 9.2 |

The high effectiveness of action of the molecule $NO_2$, which is a product of a reaction, attracts attention.

**6.3. Participation of Internal Degrees of Freedom in the Activation of a Molecule. Theories of Hinshelwood, Kassel and Slater.** It follows from Lindemann's scheme that the activation of a molecule is a bimolecular process whose rate is described by the equation

$$\frac{d[A^*]}{dt} = k[A]^2 = 2\sigma_{eff}^2 N [A]^2 \left(\frac{\pi RT}{M}\right)^{1/2} e^{-E/RT} \qquad (6.10)$$

and, consequently, the rate of a monomolecular reaction described by Eq. (6.6) may be either lower than or equal to the rate of activation. Let us check this statement with the aid of experimental data, taking as an example the decomposition of chloroethane (see Table 6.2). In the conditions of conducting the experiment at 100 mm Hg and 750 K, one cubic centimetre contains

$$\frac{100 \times 273.2}{2.24 \times 10^4 \times 760 \times 750} = 2.15 \times 10^{-6} \text{ mole of } C_2H_5Cl$$

For the effective diameter of a molecule of chloroethane at 750 K, using the data of Table 4.1 and Eq. (4.2), we get

$$\sigma_{eff}^2 = (4.98)^2 \times 10^{-16} \left(1 + \frac{366}{750}\right) = 2.72 \times 10^{-15} \text{ cm}^2$$

Let us calculate the limiting rate of a monomolecular reaction by Eq. (6.10) on the basis of the data obtained:

$$-\frac{d[C_2H_5Cl]}{dt} = k[C_2H_5Cl]^2 = (2.15 \times 10^{-6})^2 \times 2 \times 2.72 \times 10^{-15} \times$$

$$\times 6.02 \times 10^{23} \times \sqrt{\frac{3.14 \times 8.314 \times 10^7 \times 750}{64.5}}\, e^{-\frac{60\,800}{1.987 \times 750}} =$$

$$= 8.07 \times 10^4 e^{-40.8} = 1.54 \times 10^{-15} \text{ mol/s}$$

Since the experimental constant is known, Eq. (6.6) can be used to calculate the rate of the reaction:

$$-\frac{d[C_2H_5Cl]}{dt} = k[C_2H_5Cl] = 3.9 \times 10^{14} \times 2.15 \times$$

$$\times 10^{-6} e^{-\frac{60\,800}{1.987 \times 7501}} = 1.59 \times 10^{-9} \text{ mol/s}$$

Comparing the calculated and experimental values, we get

$$\frac{\text{Experimental rate}}{\text{Limiting rate}} = \frac{1.59 \times 10^{-9}}{1.54 \times 10^{-15}} \approx 10^6 \text{ times}$$

i.e. the experimental data exceed the theoretical data $10^6$ times.

Here a circumstance is uncovered that cannot in any way compromise Lindemann's scheme, but which requires the introduction of considerable clarification into the molecular-kinetic theory of bimolecular reactions. Equation (4.4) whose application to comparatively simple molecules undergoing bimolecular decomposition was justified, cannot be applied to the bimolecular decomposition of complex molecules. The matter is that this equation was deduced on the assumption that all the energy of the colliding molecules is the kinetic energy of their translational motion; in other words, the equation was deduced with account taken of two degrees of freedom, i.e. without account of the internal degrees of freedom. Since all the atoms in a polyatomic molecule are in a state of vibrational motion, a model of a molecule as a complex of a certain number of independent vibrations was found to be very useful in chemical kinetics[1]. If the energy can be distributed between $s$ vibrators of a polyatomic molecule, the number of molecules having an energy equal to or greater than the activation energy $E$ on all the internal degrees of freedom is equal to (see Sec. 3.3, 7)

$$N_a = N \frac{\left(\frac{E}{RT}\right)^{s-1}}{(s-1)!} e^{-E/RT} \tag{6.11}$$

If this is taken into consideration, then the number of collisions between molecules whose energy is equal to or greater than $E$ should be described by Eq. (6.11). Consequently, the rate of a bimolecular activation is equal to

$$\frac{d[A^*]}{dt} = [A]^2 2\sigma_{eff}^2 N \left(\frac{\pi RT}{M}\right)^{1/2} \frac{\left(\frac{E}{RT}\right)^{s-1}}{(s-1)!} e^{-E/RT} \tag{6.12}$$

It is easy to see that for diatomic molecules ($s = 1$) Eq. (6.12) transforms into the ordinary Arrhenius equation. Let us check Eq. (6.12) according to experimental data for the decomposition of chloroethane considered previously. Chloroethane is an eight-atom non-linear molecule, and the maximum number of independent vibrators

[1] For an $n$-atomic non-linear molecule the number of vibrational degrees of freedom is equal to $2n - 6$, of which $n - 5$ are deformation ones and $n - 1$ are valence ones. If we limit ourselves to the consideration of only valence vibrations, the limiting number of which is $s = n - 1$, then since (as will be shown below) we usually have to use the number of so-called effective vibrators for calculations, we have $s_{eff} \geqslant n - 1$

according to the accepted model is seven. Hence Eq. (6.12) gives

$$-\frac{d[C_2H_5Cl]}{dt} = 8.07 \times 10^4 \times \frac{(40.8)^6}{6!} e^{-40.8} = 9.89 \times 10^{-9} \text{ mol/s}$$

This result, especially in comparison with that performed according to Eq. (6.10), is quite satisfactory. Coincidence with experimental data can be considerably improved by proper selection of the number of independent vibrators. Thus, in the case being considered for $s = 6$ we get $-\frac{d[C_2H_5Cl]}{dt} = 5.82 \times 10^{-9}$ mol/s, while if we assume that $s = 5$, then $-\frac{d[C_2H_5Cl]}{dt} = 1.79 \times 10^{-9}$ mol/s, i.e. we now obtain complete coincidence with experiments. Such a somewhat arbitrary selection of the number of independent vibrators can be substantiated by the fact that at a given temperature not all the degrees of freedom participate in activation. The number of vibrators giving good coincidence with experimental data is called the *effective number of vibrators.*

It can be seen from the above that the studying of monomolecular reactions led on one hand to the generalization of bi- and monomolecular processes and to a single view to them, and on the other to a considerable broadening of the kinetic theory of an elementary bimolecular act. Further development of the theory (C. Hinshelwood, L. Kassel, W. Slater) is following the path of determining more precisely the molecular model and its relation to the kinetic properties.

*Hinshelwood's Theory.* Hinshelwood was the first to pay attention to the relation between the internal structure of a molecule and its kinetic properties and calculate the maximum rate of a monomolecular reaction according to equations similar to Eq. (6.12). Characteristic of his theory is the absence of any limitations on the transfer of energy from one vibrator to another one. In concrete calculations, as was shown above, the selection of the number of effective vibrators remains indefinite.

*Kassel's theory.* Kassel proposed a model of a molecule as a complex of $s$ vibrators having the same frequency of vibrations $\nu$. The number of vibrators $s$ for an $n$-atomic molecule is equal to $3n - 6$. The vibrators are quantized and can give up or receive from one another only energy that is a multiple of $h\nu$. Only such a molecule is considered to be capable of monomolecular decomposition in which $m$ quanta, i.e. an energy equal to $mh\nu$, are concentrated on a definite vibrational degree of freedom of it. The probability of decomposition of an active molecule is taken to be proportional to the probability of a definite concentration of the quanta on one of the vibrators, namely,

$$\begin{bmatrix}\text{Probability of}\\ \text{decomposition}\end{bmatrix} = A \begin{bmatrix}\text{Probability of concentration of}\\ m \text{ quanta on one vibrator}\end{bmatrix}$$

where $A$ is a proportionality factor.

As a result the maximum rate constant is equal to

$$k_\infty = Ae^{-E/RT} \tag{6.13}$$

where $E = mh\nu$, and in the general case for the rate constant we get the following expression

$$k_r = k_\infty (1-e^{-h\nu/kT})^s \sum_{p=0}^{\infty} \frac{\frac{(p+s-1)!}{p!\,(s-1)!} e^{-ph\nu/kT}}{1+\frac{A}{Z_0 n_A}\frac{(p+m)!\,(p+s-1)!}{p!\,(p+m+s-1)!}} \tag{6.14}$$

where $s$ = number of vibrators equal to the number of vibrational degrees of freedom of a molecule

$p$ = difference between total number of quanta which all $s$ vibrators have and the number of quanta $m$ concentrated on one vibrator.

Thus summation actually begins from a state when $m$ quanta are already concentrated, and further according to their increasing number. Consequently, according to Kassel's theory the rate depends on the excess energy in comparison with the activation energy which the reacting molecules have.

It is easy to see that neglecting unity at low pressures, and the second addend in the denominator of Eq. (6.14) at high pressures, we get the limiting kinetic laws of the second and first order respectively. Equation (6.14) also makes it possible to express the dependence of the rate constant of a reaction on the temperature and pressure more accurately than Eq. (6.9). As shown by Kassel himself on the example of calculations of data for a great number of reactions, coincidence with experimental data can be achieved by properly selecting (with a greater or smaller physical substantiation) the value of $m$. Thus, Kassel's theory also allows a selection of the numbers that is not always physically substantiated. In addition, the constant $A$ remains to be precised theoretically.

*Slater's theory.* In this theory the initial model of a molecule is a mechanical system consisting of particles joined to one another that perform harmonic vibrations about a certain position of equilibrium. The frequencies of the vibrations of the particles are different, but the exchange of energies between them is impossible without any external action. A change in the total energy of a molecule and redistribution of the energy between separate vibrating particles occur only upon a collision. The molecule in which a certain critical energy $\varepsilon$ is concentrated on a quite definite vibrator becomes active and capable of monomolecular decomposition. It is also essential that a monomolecular transformation occur before the next collision as a result of which deactivating redistribution of the vibrational energy may take place. Slater obtained the following equation for the maximum rate constant of a monomolecular reaction:

$$k_\infty = \nu e^{-E/RT} \tag{6.15}$$

where $\nu$ is the mean square frequency of all natural vibrations of a molecule, and

$$E = n_A \sum_i \varepsilon_i \tag{6.16}$$

here $\sum_i \varepsilon_i$ is the sum of the energy of all the vibrations in an activated molecule.

It should be noted that Eq. (6.15) coincides in form with the similar equation (6.13) in Kassel's theory.

If we compare the results of applying Kassel's and Slater's theories to specific cases, it will be found that the first of them is more applicable to some molecules (for example, the decomposition of $N_2O$, $H_2O_2$, $C_2H_4$), and the second to others (for example, the decomposition of $N_2O_5$, $O_3$, $C_2H_5Cl$). A comparison of the molecular models shows that according to Kassel a molecule in a reactive state must only have a definite energy, while according to Slater it must additionally have a given configuration. Hence follow the spheres of application of the two theories. In conditions of observance of the Maxwell-Boltzmann distribution (at sufficient-

ly high pressures) the number of active molecules is great, and the rate will be limited by their passing over into a form with the proper configuration and capable of reaction, i.e. Slater's theory is applicable. At low pressures, when the time interval between collisions is sufficiently great, the number of active molecules itself will be limiting, and Kassel's theory can be applied.

**6.4. Monomolecular Reactions and Theory of Activated Complex Method.** The passing over of a molecule into the active state in a monomolecular reaction can be represented as follows:

$$A + A \rightarrow A^{\star} + A$$

and the basic equation of the activated complex theory will be written as follows

$$k_r = \chi \frac{kT}{h} \frac{Q_A^{\star}}{Q_A} e^{-E_0/RT} \tag{6.17}$$

In the given case the activated complex is quite close to the initial molecule in its structure—their masses are equal and the translational partition functions are identical; the possible increase in the geometrical dimensions due to loosening of the bonds is not so great that neglection of the difference between the rotational partition functions could essentially affect the numerical results. The same considerations also hold for the symmetry numbers. From a statistical viewpoint only the vibrational partition functions differ, the vibrational partition function in the initial $n$-atomic (non-linear) molecule consisting of $3n - 6$ factors, and in the activated complex of $3n - 7$ factors. In view of the above, Eq. (6.17) can be written as follows:

$$k_r = \chi \frac{kT}{h} \frac{\prod_{i=1}^{3n-6} (1 - e^{-h\nu_i/kT})}{\prod_{i=1}^{3n-7} (1 - e^{-h\nu_i^{\star}/kT})} e^{-E_0/RT} \tag{6.18}$$

The practical use of Eq. (6.18) is hampered by the circumstance that the frequencies of vibrations in the activated complex are not known in the majority of cases. To surmount this difficulty, another assumption is made: the values of the frequencies of the vibrations in the initial molecule and in the activated complex are close. The result is that a practically applicable expression is obtained for the rate constant from Eq. (6.18):

$$k_r = \chi \frac{kT}{h} (1 - e^{-h\nu/kT}) e^{-E_0/RT} \tag{6.19}$$

where $\nu$ formally corresponds to the frequency of vibrations in the initial molecule absent in the activated complex. Let us see whether the results obtained by Eq. (6.19) correspond to experimental data,

taking as an example the decomposition of dimethyl ether:

$$CH_3OCH_3 \longrightarrow CH_4 + H_2 + CO$$

The primary elementary act is apparently decomposition along the bond C—O, for which $\omega = 940\ cm^{-1}$. Let the temperature be 750 K (the mean value in the interval from 695 to 825 K). Hence for the separate factors in the preexponential term of Eq. (6.19) we get

$$\frac{kT}{h} = \frac{1.38 \times 10^{-16}\ (erg/K)\ 750\ (K)}{6.62 \times 10^{-27}\ (erg \cdot s)} = 1.57 \times 10^{13}\ s^{-1}$$

$$\nu = c\omega = 2.99 \times 10^{10}\ (cm/s)\ 940\ (cm^{-1}) = 2.81 \times 10^{13}\ s^{-1}$$

$$\frac{h\nu}{kT} = \frac{2.81 \times 10^{13}}{1.57 \times 10^{13}} = 1.79;\ e^{-1.79} = 0.167$$

$$\frac{kT}{h}(1 - e^{-h\nu/kT}) = 1.57 \times 10^{13} \times 0.833 = 1.31 \times 10^{13}\ s^{-1}$$

The experimental value of the preexponential term (see Table 6.3) is equal to $1.9 \times 10^{13}\ s^{-1}$. Since in monomolecular reactions activation is a process of accumulation of vibrational energy on the internal degrees of freedom of a molecule and is not accompanied by a transition to an excited electron level, i.e. is essentially an adiabatic process, the transmission coefficient is close to unity, and the calculated and experimental values of the preexponential term obtained are comparable. It can be seen that in the present case a quite satisfactory coincidence has been obtained.

To appraise the possible changes in the values of the preexponential factor (the activated complex method) as applied to monomolecular reactions, let us consider two extreme cases, namely,

$$h\nu \gg kT \text{ and } h\nu \ll kT$$

If $h\nu \gg kT$, then $1 - e^{-h\nu/kT} \approx 1$, and from Eq. (6.19)

$$k_r = \chi \frac{kT}{h} e^{-E_0/RT} \tag{6.20}$$

i.e. the value of the preexponential factor coincides with the quantity $kT/h$ or, as was shown above, for the usual temperatures which monomolecular reactions are conducted at it has a value of the order of $10^{13}\ s^{-1}$.

If $h\nu \ll kT$, then limiting ourselves to the second term of the expansion of the exponent into a series, we get

$$1 - e^{-h\nu/kT} \cong \frac{h\nu}{kT} \tag{6.21}$$

and Eq. (6.19) will transform into the approximate equation

$$k_r \cong \chi\nu e^{-E_0/RT} \tag{6.22}$$

which, as can be seen, formally coincides with Eq. (6.13) in Kassel's theory and with Eq. (6.15) in Slater's theory.

The frequencies of the valence molecular vibrations $\nu = c\omega$ have the order of $10^{13}\ s^{-1}$, i.e. the same result is obtained as when calculating according to Eq. (6.20).

Thus, preexponential factors of the order of $10^{13}$ $s^{-1}$ in the kinetic equation of monomolecular reactions are satisfactorily explained by the activated complex theory. With respect to cases of sharp deviation of the preexponential factor from this value, a qualitative explanation can be given on the basis of the thermodynamic aspect of the activated complex theory. The equation relating the rate constant to the activation entropy and enthalpy has the form

$$k_r = \frac{kT}{h} e^{\Delta S^\star/R} e^{-\Delta H^\star/RT} \tag{6.23}$$

while experiments give the relation

$$k_r = Ae^{-E/RT} \tag{6.23a}$$

Hence, assuming that $kT/h \approx 10^{13}$, we obtain the approximate relation

$$A \approx 10^{13} e^{\Delta S^\star/R} \tag{6.24}$$

which allows us to determine the activation entropy

$$\Delta S^\star \approx 4.575 \log A - 59.5 \tag{6.25}$$

If calculations result in a positive change in the entropy, this points to unorderly structure of the activated complex in comparison with the structure of the initial molecule. Somewhat less convincing is the opposite statement on the increase in the orderly nature of the bonds in the activated complex when the activation entropy is negative, since the notion of an excited structure being more orderly than the initial one seems to be somewhat lacking in logic. And it is quite difficult to imagine the existence of great changes in the entropy upon the formation of an activated complex. For example, upon the decomposition of tetramethyl tin $\Delta S^\star = +38.82$ cal/K, and upon the decomposition of nitrous oxide $\Delta S^\star = -18.35$ cal/K. It is quite obvious that such changes in the activation entropy cannot be connected with the structure of the activated complex.

The factor $e^{\Delta S^\star/R}$ is the analogue of the steric factor $P$ in the theory of the method of collisions and is connected with the probability of achieving a configuration capable of reaction when the corresponding energy conditions are observed, i.e. with the problem (in addition to the structure of the activated complex) of the same mechanism of participation of all the degrees of freedom of a molecule in its activation. Thus, in the region of great deviations of experimental values from calculated ones, the theory of the activated complex method, while qualitatively solving in part the difficulties that appear, in many aspects only translates them into another

language.[1] The fact itself of the existence of a great number of theories of monomolecular decomposition and the continuous development of new theories show that meanwhile there is no quite satisfactory theory in this field.

**6.5. Trimolecular Reactions and the Collision Theory.** All homogeneous reactions of recombination of atoms and radicals with the participation of a third particle are trimolecular (termolecular) processes. The mechanism of these processes was disclosed earlier (see Sec. 2.7). Here we shall note that the part of the third particle in transferring energy from the newly formed molecule, as a rule, grows with an increase in the molecular (atomic) mass and in the number of degrees of freedom; the correctness of these criteria is violated under the influence of the specific chemical nature of the third particle.

Table 6.7 gives the rate constants for the bulk recombination of atomic oxygen

$$O + O + M \rightarrow O_2 + M$$

depending on the nature of the third particle.

TABLE 6.7

**Influence of Third Particle on Bulk Recombination of Atomic Oxygen at 273 K**

| Third particle | Atomic (molecular) mass | Oxygen recombination constants, $cm^6/mol \cdot s$ |
|---|---|---|
| Ar | 39.94 | $2.68 \times 10^{14}$ |
| Kr | 83.80 | $5.37 \times 10^{14}$ |
| Xe | 131.3 | $1.58 \times 10^{15}$ |
| O | 16 | $1.41 \times 10^{18}$ |
| $O_2$ | 32 | $4.7 \times 10^{18}$ |

The recombination constants grow regularly in the series of the inert gases (effect of the atomic mass). Upon passing over to an oxygen atom, notwithstanding the considerably smaller mass of the particle, the constant increases by three orders (this is possibly the result of the unsaturated state, which increases the probability of interaction), and for molecular oxygen the recombination constant

[1] The assumption according to which the high values of the preexponential factor are explained by the simultaneous breaking not of one, but of two or more bonds in the activated complex deserves attention. It can be shown that when this possibility is taken into account, the preexponential factor grows by several orders. An example is the decomposition of tetraalkyls of Group IV elements.

again grows three times (in addition to the increase in mass, the appearance of a vibrational degree of freedom is also of significance).

For the interaction of saturated molecules there are known only four reactions proceeding as trimolecular ones. These are the reactions of interaction of nitrogen oxide with oxygen, chlorine, bromine and hydrogen, whose kinetic data are presented in Table 6.8.

TABLE 6.8

**Kinetic Data on Trimolecular Reactions with the Participation of Nitrogen Oxide**

| Reaction | $T$, K | Rate constant, $cm^6/mol \cdot s$ |
|---|---|---|
| $2NO + O_2 \rightarrow 2NO_2$ | 273 | $8.41 \times 10^9$ |
| $2NO + Cl_2 \rightarrow 2NOCl$ | 273 | $5.70 \times 10^6$ |
| $2NO + Br_2 \rightarrow 2NOBr$ | 273 | $3.0 \times 10^9$ |
| $2NO + H_2 \rightarrow N_2O + H_2O$ (with the following step $N_2O + H_2 \rightarrow N_2 + H_2O$) | 904 | $2.65 \times 10^6$ |

The following experimental fact is the most characteristic one requiring theoretical explanation: the temperature dependence of the rate according to the Arrhenius equation is not obeyed for trimolecular reactions. Figure 6.4 shows the change in the rate constant with the temperature for the oxidation of nitrogen oxide both

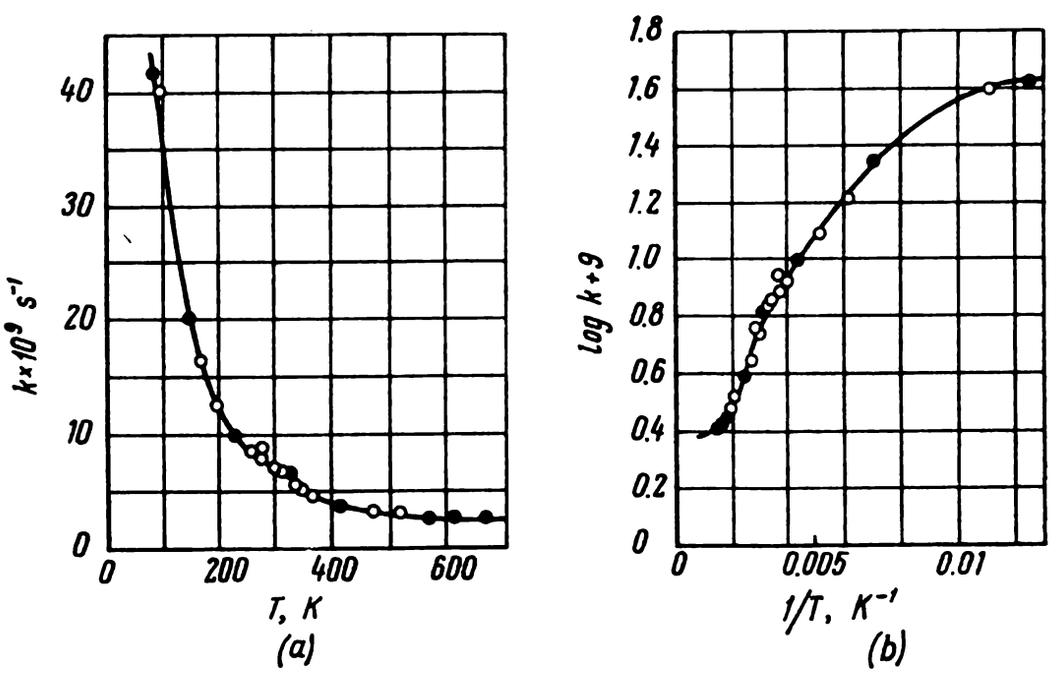



Fig. 6.4. Temperature dependence or rate of oxidation of nitrogen oxide: *a*—$k = f(T)$; *b*—$\log k = f_1(1/T)$. The white circles show calculated data, and the black ones experimental data

in the coordinates $k$ versus $T$ and in the coordinates of the Arrhenius equation log $k$ versus $1/T$. A glance at the experimental curves shows that in contrast to all the examples considered up to now, the reaction rate clearly drops with an increase in the temperature.

The first attempt to explain the mechanism of trimolecular reactions belongs to M. Trautz, who considered them as two-step processes. The first step is completely in equilibrium and, for example, for the reaction of formation of nitrosyl chloride consists in the combining of an NO molecule having an unpaired electron with a chlorine molecule:

$$NO + Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NOCl_2$$

Consequently

$$\frac{d[NOCl_2]}{dt} = k_1 [NO][Cl_2] - k_2 [NOCl_2] = 0$$

Hence we find that

$$[NOCl_2] = K [NO] [Cl_2]$$

where $K = k_1/k_2$ is the equilibrium constant.

The second, slow step determining the rate of the process as a whole is the reaction of the intermediate compound with another molecule of NO:

$$NOCl_2 + NO \xrightarrow{k} 2NOCl$$

The rate of the reaction of formation of nitrosyl chloride is

$$\frac{d[NOCl]}{dt} = k [NO][NOCl_2]$$

Inserting into this expression the value of $[NOCl_2]$, we get

$$\frac{d[NOCl]}{dt} = kK [NO]^2 [Cl_2] \tag{6.26}$$

i.e. kinetically the process is a third-order reaction.

With a growth in temperature, equilibrium shifts in the direction of the reactants, and the rate of the reaction decreases at the expense of a reduction in the concentration of the molecules $NOCl_2$. Qualitatively the same result is also obtained when considering the temperature dependence of the number of triple collisions: a growth in the temperature is accompanied by an increase in the velocity $v_{AB}$ of the colliding molecules and a reduction in the lifetime of a colliding pair $\tau_{AB}$. Thus, the number of triple collisions should decrease somewhat with the temperature. Theoretical calculations, however, do not coincide with experimental data.

An attempt was made to improve the result obtained according to the formula for the number of triple collisions by taking into account the interaction between the molecules. In the present case this is quite essential, since with attraction between the molecules the lifetime of a colliding pair may considerably increase. This naturally leads to a growth in the number of triple collisions. In addition, with a growth in the temperature the role of the interaction decreases, which cannot fail to affect the temperature dependence of the reaction rate. If we assume a sphere model of a molecule with a central spherical force field, then, as has been noted, the interaction can be taken into account by multiplying the corresponding equations for an ideal gas by the factor $1 + \frac{\varphi_0}{RT}$ proposed by W. Sutherland (where $\varphi_0$ is a certain constant related to the energy of interaction). Hence the number of triple collisions will be

$$Z_{3,\ \text{non-ideal}} = \left(1 + \frac{\varphi_0}{RT}\right) Z_{3,\ \text{ideal}} \tag{6.27}$$

and instead of the van't Hoff-Arrhenius equation

$$\frac{d \ln Z_3}{dT} = \frac{E}{RT^2} \tag{6.28}$$

we get the equation

$$\frac{d \ln Z_3}{dT} = -\frac{\varphi_0}{T(RT + \varphi_0)} + \frac{E}{RT} \tag{6.29}$$

that gives a relation similar to the curve in Fig. 6.4*b*. The indefiniteness of the constant $\varphi_0$ makes quantitative calculations quite unreliable, however, and for this reason many investigators limit themselves to giving empirical temperature dependences of the rate constant, for example for the reaction $2NO + Cl_2$ we have $\log k = \frac{490}{T} + 10.51 \log T - 20.697$; for the reaction $2NO + H_2$ we have $\log k = \frac{38\,689 \times 2}{T} - 66.37 \log T + 245.410$.

**6.6*. Trimolecular Reactions and the Activated Complex Theory.** The main difficulty in applying the transition-state theory to trimolecular reactions is the absence of information on the composition, configuration and properties of the activated complex. Consequently, what remains is to accept the most verisimilar form of the activated complex and on the basis of this model to compute the corresponding partition functions and compare the results obtained with experimental data. Let us consider this approximate method on the example of the oxidation of nitrogen oxide:

$$2NO + O_2 \rightleftarrows 2NO_2$$

It is considered that the activated complex consists of all the molecules participating in the reaction, i.e. has the composition $(NO)_2O_2$. Its hypothetical structure is as follows:

```
O=N---O
      ⋮
O=N---O
```

The direction of the valences in the oxygen and nitrogen oxide molecules underlies the rectangular configuration. Consequently, the activated complex has four translational degrees of freedom, one of which is already taken into account in the basic equation of the theory, three rotational and $3 \times 6 - 7 = 11$ vibrational degrees of freedom. In connection with the structure, however, one vibrational degree of freedom is replaced by a rotational one along the bond O—O, and for this reason 10 vibrational degrees of freedom remain, and the factor

$(8\pi^2 I_{OO}kT/h^2)^{1/2}$ appears (here $I_{OO}$ is the moment of inertia about the axis of the bond O—O). Hence the partition function of the activated complex is

$$Q^\star = g^\star \underbrace{\frac{(2\pi\mu^\star kT)^{3/2}}{h^3}}_{\text{translational component}} \underbrace{\frac{8\pi^2\,(8\pi^3 I_x I_y I_z)^{1/2}\,(kT)^{3/2}}{\sigma^\star h^3}\,\frac{(8\pi^2 I_{OO}kT)^{1/2}}{h}}_{\text{rotational component}} \times$$

$$\times \underbrace{\prod_{i=1}^{10}\left(1-e^{-\frac{h\nu_i^\star}{kT}}\right)^{-1}}_{\text{vibrational component}} \tag{6.30}$$

where $g^\star$ = electron multiplicity of activated complex
$\mu^\star$ = reduced mass
$I_x I_y I_z$ = product of principal moments of inertia
$\sigma^\star$ = symmetry factor
$\nu_i^\star$ = frequency of vibrations of activated complex.

Assuming that $\chi = 1$, from Eq. (4.22) we get the following expression for the rate constant:

$$k_r = \frac{kT}{h}\,\frac{Q^\star}{Q_{O_2}Q_{NO}^2}\,e^{-E_0/RT} = \frac{g^\star}{g_{O_2}g_{NO}^2}\,\frac{kT}{h} \times$$

$$\times \frac{\dfrac{(2\pi\mu^\star kT)^{3/2}}{h^3}\,\dfrac{8\pi^2\,(8\pi^3 I_x I_y I_z)^{1/2}\,(kT)^{3/2}}{\sigma^\star h^3}\,\dfrac{(8\pi^2 I_{OO}kT)^{1/2}}{h}}{\dfrac{(2\pi m_{O_2}kT)^{3/2}}{h^3}\,\dfrac{(2\pi m_{NO}kT)^3}{h^6}\,\dfrac{(8\pi^2 I_{O_2}kT)}{\sigma_{O_2}h^2}\,\dfrac{(8\pi^2 I_{NO}kT)^2}{\sigma_{NO}^2 h^4}} \times$$

$$\times \frac{\prod_{i=1}^{10}\left(1-e^{-h\nu_i^\star/kT}\right)^{-1}\,e^{-E_0/RT}}{\left(1-e^{-h\nu_{O_2}/kT}\right)^{-1}\left(1-e^{-h\nu_{NO}/kT}\right)^{-2}} \tag{6.31}$$

where $g_{O_2}$ and $g_{NO}$ = electron multiplicities of $O_2$ and NO
$\sigma_{O_2} = 2$ and $\sigma_{NO} = 1$ = respective symmetry factors
$m_{O_2}$ and $m_{NO}$ = masses of $O_2$ and NO
$I_{O_2}$ and $I_{NO}$ = moments of inertia
$\nu_{O_2}$ and $\nu_{NO}$ = fundamental frequencies of vibration of oxygen and nitrogen oxide.

Let us combine into a separate factor all the quantities that do not depend on the temperature:

$$G = \frac{g^\star}{g_{O_2}g_{NO}^2}\,\frac{\pi^{3/2}h^3}{16}\left(\frac{h}{2\pi k}\right)^3 \frac{\mu^{\star 3/2}\,(I_x I_y I_z I_{OO})^{1/2}}{\sigma^\star m_{O_2}^{3/2} m_{NO}^3 I_{O_2} I_{NO}^2} \tag{6.32}$$

Hence Eq. (6.31) becomes

$$k_r = G\frac{1}{T^3}\,\frac{\prod_{i=1}^{10}\left(1-e^{-h\nu_i^\star/kT}\right)^{-1}}{\left(1-e^{h\nu_{O_2}/kT}\right)^{-1}\left(1-e^{-h\nu_{NO}/kT}\right)^{-2}}\,e^{-E_0/RT} \tag{6.33}$$

TABLE 6.9

**Comparison of Calculated and Experimentally Obtained Values of $k_r$ at Different Temperatures for the Reaction $2NO+O_2=2NO_2$**

| $T$, K | $k_r \times 10^9$, cm$^6$/mol$^2\cdot$s | |
|---|---|---|
| | calculated | experimental (according to M. Bodenstein) |
| 80 | 86.0 | 41.8 |
| 143 | 16.2 | 20.2 |
| 228 | 5.3 | 10.1 |
| 300 | 3.3 | 7.1 |
| 413 | 2.2 | 3.2 |
| 564 | 2.0 | 2.8 |
| 613 | 2.1 | 2.8 |
| 662 | 2.1 | 2.9 |

Before passing over to quantitative calculations, let us note that, as follows from Eq. (6.33), the rate of a trimolecular reaction should decrease quite noticeably with elevation of the temperature; the rate constant is inversely proportional to the third power of the temperature.

To practically use Eq. (6.33) we must know the frequencies of vibrations $\nu_i^*$ of the activated complex. It was proposed to use the vibration frequencies of a molecule of $N_2O_4$ having the same composition as the activated complex, but an absolutely different structure. Of the ten natural frequencies of $N_2O_4$ only six must be taken into account (680, 283, 752, 500, 380, and 813 cm$^{-1}$), i.e. those that are less than 900 cm$^{-1}$; and for the remaining ones (1380, 1265, 1724 and 1749 cm$^{-1}$) we can assume for practical purposes that $(1-e^{-h\nu/kT})$ is approximately equal to unity. The same relates to the natural frequencies of vibrations of molecules of oxygen (1580.32 cm$^{-1}$) and nitrogen oxide (1906.54 cm$^{-1}$). Thus, having simplified Eq. (6.33), we get it in a form convenient for calculations:

$$k_r=\frac{G}{T^3}\prod_{i=1}^{6}\left(1-e^{-h\nu_i^*/kT}\right)^{-1}e^{-E_0/RT}=\frac{4.45}{T^3}\prod_{i=1}^{6}\left(1-e^{-h\nu_i^*/kT}\right)^{-1}e^{-E_0/RT} \quad (6.34)$$

Grouping the addends and taking logarithms, we get

$$\ln k_r+3\ln T-\ln\prod_{i=1}^{6}\left(1-e^{-h\nu_i^*/kT}\right)=\ln k_r+f(T)=\ln G-\frac{E_0}{RT} \quad (6.35)$$

where

$$f(T)=3\ln T-\ln\prod_{i=1}^{6}\left(1-e^{-h\nu_i^*/kT}\right) \quad (6.36)$$

To determine the activation energy, it is sufficient to plot a chart of the relation

$$\ln k_r+f(T)=f_1\left(\frac{1}{T}\right) \quad (6.37)$$

according to experimental data and the calculated value of $\prod_{i=1}^{6} (1 - e^{-h\nu_i^{\star}/kT})$ and find the activation energy according to the tangent of the angle of inclination of the straight line obtained.

The corresponding graphical calculation shows that upon the oxidation of NO the activation energy is practically equal to zero. Knowing the activation energy, Eq. (6.35) can be used to calculate the theoretical value of the rate constant at different temperatures. The results of the calculation, in which experimental points are used (the black circles in Fig. 6.4), are compared with the experimental data in Table 6.9.

The coincidence of the theoretical values with the experimental ones is quite good. A better coincidence could be obtained if the values of certain frequencies were arbitrarily changed, but there is no physical substantiation for this.

In summarizing, the conclusion can be drawn from what has been discussed above that notwithstanding a number of arbitrary assumptions in quantitative verification, the activated complex theory solves the main theoretical difficulties appearing in the consideration of trimolecular reactions, in particular, it explains the anomalous temperature dependence of the reaction rate.

CHAPTER 7

# REACTIONS IN SOLUTIONS

**7.1. Application of Theoretical Ideas Developed for Reactions in a Gaseous Phase to Reactions in Solutions.** The theory of the liquid state has been worked out to a much lower extent than that of the gaseous state, and this has an appreciable influence on the level of theoretical interpretation of chemical kinetics in a condensed phase. The theory of reactions in a gaseous phase is based on two corollaries of the molecular-kinetic theory, namely, the possibility of calculating the number of collisions between reacting molecules and the applicability of the Maxwell-Boltzmann distribution to a reacting system. When going over to reactions in solutions it becomes necessary to consider a third object—the molecules of the solvent. Here two extreme cases are possible: (1) the molecules of the solvent do not enter the composition of the activated complex, and their interaction with the molecules of the solute consists in collisions and van der Waals interaction; (2) the molecules of the solvent enter the composition of the activated complex and to a certain extent determine the kinetic properties of the latter. Interaction of the second kind most likely relates more to catalytic phenomena and will be considered later. Limiting ourselves to the first case, let us see to what extent the methods of the kinetic theory for reactions in a gaseous phase are applicable to reactions in solutions. May we use the gas-kinetic equation to count the number of collisions between reacting molecules in solutions? It is difficult to give a substantiated reply to this question, and we shall have to limit ourselves to a criterion of the practical applicability of such calculations. Since in studying reactions in solutions it is convenient to use the values of the concentrations expressed in mol/dm$^3$, the gas-kinetic equation for the rate constant will be written in the following form:

$$k = P\frac{N}{1000}\sigma_{AB}^2\left[8\pi RT\left(\frac{1}{M_A}+\frac{1}{M_B}\right)\right]^{1/2}e^{-E/RT} \qquad (7.1)$$

where all the symbols are similar to those in Eq. (4.9), and the factor $10^{-3}$ has been introduced for the rate constant to have the dimensions dm$^3$/mol·s. The applicability of Eq. (7.1) can be appraised as follows. Taking the experimental value of the rate constant for a bimolecular reaction, we equate it to the value obtained from

Eq. (7.1) and calculate the value of the effective diameter of collisions $\sigma_{AB}$. The obtaining of a physically explainable value points to the practical applicability of equations of type (7.1). Let us consider as an example the reaction between sodium ethylate and ethyl iodide proceeding at room or somewhat higher temperatures in a solution of dehydrated ethyl alcohol:

$$C_2H_5ONa + C_2H_5I \rightarrow (C_2H_5)_2O + NaI$$

Experiments give the following expression for the rate constant:

$$k = 1.5 \times 10^{11} e^{-20\,650/RT} \text{ dm}^3/\text{mol}\cdot\text{s}$$

whence

$$\frac{N}{1000}\sigma_{AB}^2 \sqrt{8 \times 3.14 \times 8.314 \times 10^7 \times 298 \left(\frac{1}{68} + \frac{1}{156}\right)} = 1.5 \times 10^{11}$$

or

$$\sigma_{AB} = \sqrt{\frac{1.5 \times 10^{14}}{6.02 \times 10^{23} \sqrt{8 \times 3.14 \times 8.314 \times 10^7 \times 298 \times 2.092 \times 10^{-2}}}} =$$
$$= 4.68 \times 10^{-8} \text{ cm}$$

The result obtained is quite reasonable and in the present case allows us to reach the conclusion on the close proximity of the steric factor to unity. Similar results have been obtained for many other reactions in solutions. Exceptions are also encountered, however, but as a rule they do not lead to any doubts as to the practical applicability of Eq. (7.1).

If we consider that Eq. (7.1) allows us to obtain practically satisfactory results, then we must deal with another factor that distinguishes reactions in solutions from ones in a gaseous phase. In addition to collisions between the dissolved molecules, collisions also occur between them and the molecules of the solvent. Approximate calculations show that the number of collisions with solvent molecules exceeds that between the molecules of the reactants $10^3$ to $10^4$ times. Obviously, the rates of activation and deactivation of the dissolved molecules grow approximately the same number of times. Consequently, the Maxwell-Boltzmann distribution is not only observed for reactions in solutions, but is found to be still more stable than for reactions in a gaseous phase. It can therefore be expected that all the relations deduced on the basis of this distribution should also hold for reactions in a condensed phase. In particular, experiments show that the Arrhenius equation is also true for reactions in solutions.

What has been said above allows us to compare the same reactions proceeding in a gaseous phase and in a solution. It should be remembered here that the mechanism of a reaction sometimes changes upon

passing over to a condensed phase, and therefore such a comparison loses its sense.

For example, the bimolecular reaction between nitrogen dioxide and chlorine oxide in the gaseous phase follows the equation

$$2NO_2 + Cl_2O \rightleftharpoons NOCl + NO_2Cl + O_2$$

In the condensed phase one of the reactants dimerizes, and the reaction proceeds in a different direction, namely,

$$N_2O_4 + 2Cl_2O \rightleftharpoons 2NO_3Cl + Cl_2$$

If the reactants and the reaction mechanism do not change in passing over to a solution, a comparison is quite permissible. Let us consider, for example, the decomposition of ethyl diiodide whose mechanism complies with the equation of a bimolecular reaction:

$$C_2H_4I_2 \rightarrow C_2H_4 + I_2$$

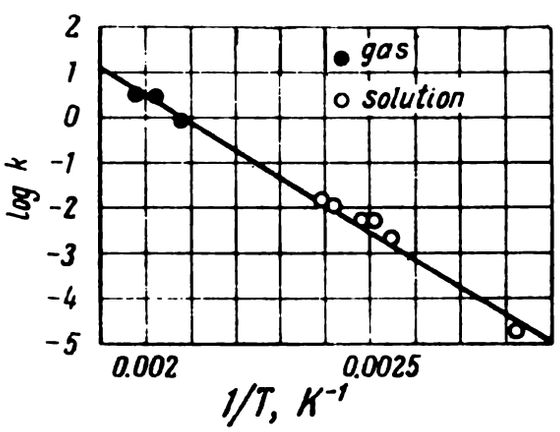



Fig. 7.1. Dependence of log $k$ on $1/T$ for decomposition of ethyl diiodide $C_2H_4I_2$

Figure 7.1 shows experimental points characterizing the relation between log $k$ and $1/T$ for this reaction in a gaseous phase and in solution in carbon tetrachloride. It can be seen that both groups of points are on one straight line. This example indicates not only that the Arrhenius equation is observed, but that if the reaction mechanism does not change, the reaction rate in both cases can be described by the same values of the parameters, i.e. the values of the activation energy and the preexponential factor do not change.

Let us see what results are obtained if we apply the activated complex theory to reactions in solutions.

For a bimolecular reaction in a gaseous phase

$$A + B \rightarrow AB^{\star} \rightarrow \text{Products}$$

the rate constant according to the activated complex theory is

$$k_{gas} = \chi \frac{kT}{h} K_{gas} = \chi \frac{kT}{h} \frac{c_{AB^{\star}}}{c_A c_B} \tag{7.2}$$

For a solution the equilibrium constant is determined by the equation

$$K_{sol} = \frac{a_{AB^{\star}}}{a_A a_B} = \frac{c_{AB^{\star}}}{c_A c_B} \frac{\gamma_{AB^{\star}}}{\gamma_A \gamma_B} \tag{7.3}$$

where $a$ = activity

$\gamma$ = activity coefficient.

On the basis of Eq. (7.3), by analogy with Eq. (7.2), we get

$$k_{sol} = \chi \frac{kT}{h} K_{sol} = \chi \frac{kT}{h} \frac{c_{AB^*}}{c_A c_B} \frac{\gamma_{AB^*}}{\gamma_A \gamma_B} \tag{7.4}$$

A comparison of Eqs. (7.2) and (7.4) shows that the value of the rate constant of a reaction in a solution should differ from the rate constant of a reaction in a gaseous phase by a factor containing the activity coefficients, i.e.

$$k_{sol} = k_{gas} \frac{\gamma_{AB^*}}{\gamma_A \gamma_B} \tag{7.5}$$

To appraise the change in the values of the rate constant when passing over from a gaseous phase to a solution with the aid of this equation, deduced by J. Bronsted and N. Bjerrum, an expression for the activity coefficients should be used. The following equation for the activity coefficient proposed by I. Langmuir can be employed to appraise the interaction between neutral particles:

$$\gamma = \beta T^{1/2} e^{-\Delta H/RT} \tag{7.6}$$

where $\beta$ = constant (equal to about 5 for unassociated liquids)
$\Delta H$ = heat of vaporization.

Inserting Eq. (7.6) into Eq. (7.5), we get

$$k_{sol} = k_{gas} \frac{\beta_{AB^*}}{\beta_A \beta_B} T^{-1/2} e^{-\frac{(\Delta H_A + \Delta H_B - \Delta H^*_{AB})}{RT}} \tag{7.7}$$

It follows from Eq. (7.7) that there may be certain discrepancies in the values of the constants being compared depending on the properties of the activated complex. Since the value of $\Delta H_A + \Delta H_B - \Delta H_{AB^*}$ will hardly exceed several thousand calories, the activation energies in the gaseous phase and the solution should not differ appreciably. The preexponential factor may change several times, however, depending on the values of $\beta_A$, $\beta_B$ and $\beta_{AB^*}$.

**7.2. Monomolecular Reactions in Solutions.** The degree of stability of the Maxwell-Boltzmann distribution of the dissolved molecules is of great significance for monomolecular reactions. It can be expected qualitatively that the kinetic characteristics of a monomolecular reaction (if, of course, the reaction mechanism does not change) should not change appreciably when the reaction is transferred to a solution or the condensed state. The activated complex theory allows us to make even more definite conclusions. Indeed, Eq. (7.7) for the monomolecular reaction

$$A \rightarrow A^* \rightarrow \text{Products}$$

can be written in the form

$$k_{sol} = k_{gas} \frac{\beta_{A^*}}{\beta_A} e^{-\frac{(\Delta H_A - \Delta H_{A^*})}{RT}} \tag{7.8}$$

It is hard to expect a noticeable difference both between $\beta_A$ and $\beta_{A^*}$ and between $\Delta H_A$ and $\Delta H_{A^*}$. For this reason monomolecular reactions should depend less than other ones on the nature of the medium in which the process proceeds. In general this is confirmed by experiments. Table 7.1 gives data on the monomolecular decomposition of nitrogen pentoxide in the gaseous phase and in solutions in different solvents, both organic and inorganic. The maximum changes in the activation energy exceed the activation energy of the reaction in the gaseous phase by not more than 1000 cal, i.e. do not exceed the limiting error of experiments. The preexponential factors change a maximum of six times in comparison with their values for a reaction in a gaseous phase.

TABLE 7.1

**Comparison of Kinetics of Monomolecular Decomposition of Nitrogen Pentoxide in the Gaseous Phase and in Selected Solvents**

| Solvent | Rate constant, $s^{-1}$ | $k_{sol}/k_{gas}$ at 20 °C |
|---|---|---|
| Gaseous phase | $4.5 \times 10^{13}\ e^{-24\,500/RT}$ | 1.00 |
| $CH_3NO_2$ | $3.1 \times 10^{13}\ e^{-24\,500/RT}$ | 0.81 |
| $Br_2$ | $2.5 \times 10^{13}\ e^{-24\,000/RT}$ | 1.14 |
| $CHCl_2CCl_3$ | $10.4 \times 10^{13}\ e^{-25\,000/RT}$ | 1.16 |
| $CCl_4$ | $2.8 \times 10^{13}\ e^{-24\,100/RT}$ | 1.24 |
| $CH_2ClCH_2Cl$ | $4.1 \times 10^{13}\ e^{-24\,400/RT}$ | 1.26 |
| $CHCl_3$ | $6.4 \times 10^{13}\ e^{-24\,600/RT}$ | 1.45 |
| $CH_3CHCl_2$ | $12.5 \times 10^{13}\ e^{-24\,900/RT}$ | 1.70 |
| $N_2O_4$ | $16.3 \times 10^{13}\ e^{-25\,000/RT}$ | 1.82 |

Table 7.2 compares data on the kinetics of monomolecular decomposition of *o*-nitrophenyl azide in selected solvents with data on the kinetics of this reaction in the condensed phase. It follows from the table that here also the changes in the activation energy do not exceed 600 cal, and the preexponential factors vary not more than 2.5 times.

TABLE 7.2

**Kinetics of Monomolecular Decomposition of *o*-Nitrophenyl Azide in the Condensed Phase and in Selected Solvents**

| Solvent | Rate constant, $s^{-1}$ |
|---|---|
| Pure liquid *o*-nitrophenyl azide | $6.2 \times 10^{12}\ e^{-26\,000/RT}$ |
| Di-*n*-butyl phthalate | $2.7 \times 10^{12}\ e^{-26\,300/RT}$ |
| Cyclohexanol | $2.4 \times 10^{12}\ e^{-26\,300/RT}$ |
| *n*-Heptane | $3.4 \times 10^{12}\ e^{-26\,600/RT}$ |

**7.3. Bimolecular Reactions in Solutions.** As indicated above, the collision theory well agrees with experimental data for many bimolecular reactions. Calculation of the effective collision diameter similar to that made in Sec. 7.1 for the reaction between sodium ethylate and ethyl iodide also gives satisfactory values of $\sigma_{AB}$ for a number of reactions. Table 7.3 gives examples of the calculations for some other reactions in which sodium methylate and ethylate participate.

TABLE 7.3

**Effective Diameter of Collisions Obtained from Kinetic Data for Selected Reactions**

| Reaction | Solvent | Rate constant, $dm^3/mol \cdot s$ | $\sigma_{AB} \times 10^8$, cm |
|---|---|---|---|
| $CH_3ONa + CH_3Cl$ | $CH_3OH$ | $1.76 \times 10^{12}\ e^{-23\,990/RT}$ | 2.53 |
| $CH_3ONa + CH_3Br$ | $CH_3OH$ | $1.74 \times 10^{12}\ e^{-21\,830/RT}$ | 2.76 |
| $CH_3ONa + CH_3I$ | $CH_3OH$ | $2.01 \times 10^{12}\ e^{-21\,940/RT}$ | 3.03 |
| $CH_3ONa + (CH_3)_2SO_4$ | $CH_3OH$ | $2.53 \times 10^{12}\ e^{-20\,820/RT}$ | 3.47 |
| $C_2H_5Na + C_2H_5I$ | $C_2H_5OH$ | $1.5 \times 10^{12}\ e^{-20\,650/RT}$ | 4.68 |
| $C_2H_5Na + C_3H_7I$ | $C_2H_5OH$ | $3.5 \times 10^{12}\ e^{-22\,450/RT}$ | 8.15 |

For bimolecular reactions a change in the initial concentration may also lead to an appreciable change in the rate constant. As a rule, a growth in the concentration results in a lower rate constant. Exceptions from this rule are encountered, however, in particular

the constant may not depend on the initial concentration. Figure 7.2 gives examples of both relations encountered: a reduction in the rate constant with an increase in concentration (the reaction of sodium ethylate with methyl iodide in an alcohol solution $C_2H_5ONa + ICH_3 \rightarrow C_2H_5OCH_3 + NaI$), and a constant value of the rate constant [the reaction of sodium ethylate with *n*-dinitrobenzene also in an alcohol solution $2C_2H_5ONa + n\text{-}C_6H_4(NO_2)_2 \rightarrow n\text{-}C_6H_4(OC_2H_5)_2 + 2NaNO_2$].

Up to now we considered cases when the applicability of the collision theory did not raise any doubts, since the expected results were obtained as a rule. There are reactions, however, for which the calculated and experimental data do not coincide so well. Let us consider one of such reactions, which was discovered and investigated kinetically in detail at the end of the 19th century by N. Menshutkin. This is the reaction of combination of an alkyl halide and tertiary amine:

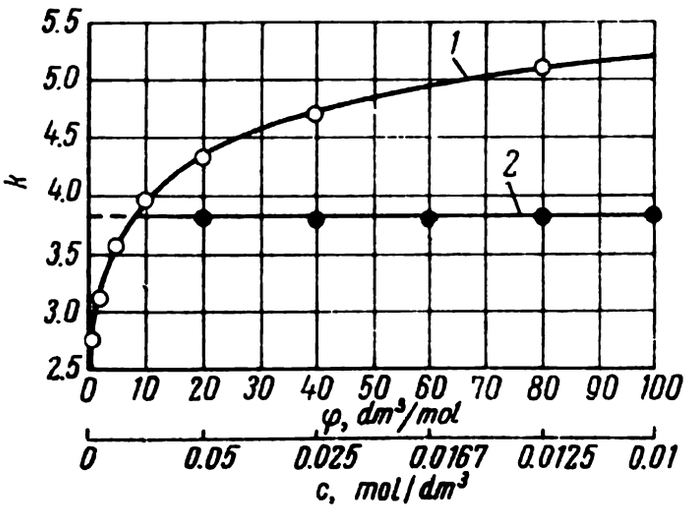



Fig. 7.2. Dependence of rate constants of reactions on dilution of solution:
1—$C_2H_5ONa + ICH_3 \rightarrow C_2H_5OCH_3 + NaI$; 2—$C_2H_5ONa + n\text{-}C_6H_4(NO_2)_2 \rightarrow n\text{-}C_6H_4(OC_2H_5)_2 + 2NaNO_2$

$$RX + (R_1)(R_2)(R_3)N \rightarrow R(R_1)(R_2)(R_3)NX$$

where X = Cl, Br, I.

Menshutkin devoted special attention to the influence of the solvent on the rate of the reaction. He established two facts: firstly, these reactions are kinetically bimolecular ones, as follows from the stoichiometric equation; secondly, the rate of each given reaction depends to a considerable extent on the chemical nature of the solvent. The application of the collision theory to Menshutkin's reactions immediately made it possible to establish an exceedingly interesting fact, namely, that only a small fraction of the active collisions leads to a reaction. Let us calculate as an example the effective collision diameter for the reaction of triethyl amine with ethyl bromide in a solution of acetone. The value of the rate constant obtained experimentally for this reaction is $k = 8.5 \times e^{-11\,710/RT}$ dm³/mole·s. Hence the effective collision diameter

$$\sigma_{AB} = \sqrt{\frac{8.5 \times 10^3}{6.02 \times 10^{23}\sqrt{8 \times 3.14 \times 8.314 \times 10^7 \times 298 \times 1.91 \times 10^{-2}}}} =$$

$$= 3.6 \times 10^{-13} \text{ cm}$$

The result obtained obviously has no physical meaning. There are also no special grounds to be doubtful of the possibility of applying the collision theory to the reaction

$$(C_2H_5)_3N + C_2H_5Br \rightarrow (C_2H_5)_4NBr$$

It therefore becomes necessary to consider that the steric factors have a very low value for Menshutkin's reactions. In particular, for the reaction considered above a reasonable value of the effective diameter of collisions is obtained if we assume that $P = 1.6 \times 10^{-8}$, i.e. only one of one hundred million active collisions leads to a reaction.

Table 7.4 contains data for three different reactions in solutions. The influence of the solvent on the rate of a reaction is quite appreciable. For the first reaction in Table 7.4, replacement of the benzene solution with acetone leads to an increase in the rate by 30 times, and for the second reaction the replacement of nitrobenzene with benzyl alcohol increases the rate 270 times. The influence of the solvent on the activation energy is less appreciable, but nevertheless the maximum difference for the second reaction is 1380 cal. The values of the steric factors are quite significant. The greatest of them has a value of the order of $10^{-5}$ and the other ones of the order of $10^{-8}$.

TABLE 7.4

**Kinetic Data on Selected Menshutkin Reactions**

| Reaction | Solvent | Rate constant, dm³/mol·s | $P$ |
|---|---|---|---|
| $(C_2H_5)_3N + C_2H_5Br$ | $C_6H_6$ | $0.28\ e^{-11\,190/RT}$ | $5.3 \times 10^{-10}$ |
| | $CH_3COCH_3$ | $8.5\ e^{-11\,710/RT}$ | $1.6 \times 10^{-8}$ |
| | $50\%C_6H_6 + 50\%CH_3COOCH_3$ | $7.2\ e^{-12\,040/RT}$ | $1.4 \times 10^{-8}$ |
| $C_6H_5(CH_3)_2N + CH_3I$ | $C_6H_5NO_2$ | $2.6 \times 10\ e^{-13\,020/RT}$ | $5.3 \times 10^{-8}$ |
| | $C_2H_2Cl_4$ | $2.1 \times 10\ e^{-11\,680/RT}$ | $4.8 \times 10^{-8}$ |
| | $C_6H_5CH_2OH$ | $7.0 \times 10^3\ e^{-14\,400/RT}$ | $1.7 \times 10^{-5}$ |
| $C_6H_5(CH_3)_2N + C_2H_5I$ | $CH_3COCH_3$ | $2.7 \times 10\ e^{-13\,680/RT}$ | $6.3 \times 10^{-8}$ |

There may be several reasons for such small values of the steric factor. It is assumed that first of all special orientation is required in a collision; in addition, the distribution of the energy between the internal degrees of freedom of each of the reacting molecules should correspond to a definite configuration. If this assumption is accepted, a value coinciding with the experimental one is obtained

for the steric factor. But, firstly, the authenticity of the assumptions made is not great, and, secondly, the part played by the solvent is not clear.

The activated complex theory gives a qualitative explanation of reactions in solutions on the basis of interaction between the active components of a system (the initial molecules and the activated complex) and the solvent molecules. For example, solvation of the reactants by the solvent leads to an increase in the activation energy, while solvation of the activated complex to its reduction by the magnitude of the energy of solvation. Without detracting in any way from the significance of this explanation, we must note that the changes in the activation energy when solvents are changed do not at all have such values which would allow us to ascribe the observed deviations of the experimental values from the theoretical ones entirely to this effect. As a whole the difficulties connected with an explanation of the kinetic laws of Menshutkin's reactions have not yet been surmounted.

**7.4. Conjugated Reactions.** If several reactions proceed simultaneously in a system, and some of them are possible only on condition that other reactions proceeding independently take place, they are called *conjugated reactions.*

For example, oxygen readily oxidizes sodium sulphite $Na_2SO_3$, but does not oxidize $Na_2HAsO_3$ when these substances are taken separately. If their mixture is taken, however, they are both easily oxidized by oxygen. Thus, the reaction of oxidation of $Na_2SO_3$ proceeding in a system causes the reaction of oxidation of $Na_2HAsO_3$. Or, for example, hydrogen peroxide oxidizes a ferrous salt, but does not interact with hydrogen iodide in an aqueous solution. If hydrogen iodide is added to a mixture of ferrous sulphate and hydrogen peroxide, however, the hydrogen iodide will be oxidized simultaneously with the reaction of oxidation of the ferrous sulphate.

A solution of indigo does not decolourize under the action of oxygen. If we add benzaldehyde to the solution, however, it will be oxidized by the oxygen to benzoic acid, the indigo will simultaneously be oxidized to isatin, and the solution will decolourize.

In the examples considered above we had such systems of two reactions proceeding in one phase in which the course of one depends on the other, i.e. a spontaneous (primary) reaction causes or accelerates a non-spontaneous (secondary) process. This phenomenon is called *chemical induction.*

Thus, in the simplest case conjugated reactions can be written in the following form:

$$A + B \quad \text{Primary reaction}$$

$$A + C \quad \text{Secondary reaction}$$

The substance participating in both the primary and secondary reactions (substance A) is called an *actor*. The substance participating only in the primary reaction (substance B) and which by its interaction with the actor causes the secondary process is called an *inductor*. The substance participating only in the secondary reaction (substance C), i.e. receiving the effect of the primary reaction, is called an *acceptor*. In chemical induction, in contrast to catalysis, the concentration of all the reactants in the course of the reactions decreases.

Conjugated reactions are possible only if the intermediate products of the first reaction are actually initial ones for the second reaction, interacting with the acceptor. The intermediate serves as a link between the primary and secondary processes and causes both of them to proceed. For example, bromic acid $HBrO_3$ directly oxidizes $H_2SO_3$, but does not oxidize $H_3AsO_3$. If we take a mixture of sulphurous and ortho-arsenous acids, however, the bromic acid will oxidize both acids.

This can be explained if we consider the reaction of oxidation of sulphurous acid by steps:

$$HBrO_3 + H_2SO_3 \rightarrow H_2SO_4 + HBrO_2$$

$$HBrO_2 + H_2SO_3 \rightarrow H_2SO_4 + HBrO$$

$$HBrO + H_2SO_3 \rightarrow H_2SO_4 + HBr$$

The intermediates $HBrO_2$ and $HBrO$ oxidize the ortho-arsenous acid. Here $HBrO_3$ is the actor, $H_2SO_3$ the inductor and $H_3AsO_3$ the acceptor.

An important quantity characterizing conjugated reactions is the *induction factor*. Introduced by N. Shilov, who has greatly contributed to the investigation of this type of reactions, the induction factor is determined by the ratio

$$I = \frac{\Delta c_{acc}}{\Delta c_{ind}} \tag{7.9}$$

where $\Delta c_{acc}$ = reduction in the concentration of the acceptor
$\Delta c_{ind}$ = reduction in the concentration of the inductor.

Since the participation of the inductor in the reaction leads to the appearance in the system of an intermediate causing the second reaction (the reaction of transformation of the acceptor), the induction factor can also be defined as

$$I = \frac{\text{reduction in initial product}}{\text{reduction in intermediate product}} \tag{7.10}$$

Three types of conjugated reactions can be distinguished depending on the value of the induction factor.

1. If partial regeneration of the inductor or intermediate occurs as a result of an induced reaction, then the amount of the initial substance (acceptor) entering into the reaction will increase and, consequently, the induction factor will be greater. In the limiting case, when the intermediate is completely regenerated, the denominator of Eq. (7.10) will become zero and the induction factor will become equal to infinity ($I = \infty$). Such a type of process is a stationary one. In practice, as we shall see later, catalytic processes and stationary unbranching chain reactions correspond to such processes.

2. If the concentration of the inductor or intermediate decreases as a result of a reaction, the process is obviously an attenuating one, i.e. its rate reduces. Here the induction factor is greater than unity ($I > 0$).

3. If the concentration of the inductor or intermediate grows as a result of the reaction, so-called self-induction is observed, characterized by an initial *self-acceleration*. This type of process includes self-inductive processes proceeding with an initial acceleration and, as we shall see later, branching chain processes. Since here the concentration of the inductor or intermediate grows, the induction factor will be less than zero ($I < 0$).

The phenomenon of chemical induction is interesting in that the free energy liberated in the spontaneous reaction in which the inductor participates may compensate for the expenditure of energy required for the formation of substances with a greater store of free energy.

The spontaneous reaction of oxidation of arsenic trioxide by bromic acid studied by Shilov is of interest in this respect. For this reaction to be possible, hydrogen bromide must be present in the system. When a mixture of $HBrO_3$ and $As_2O_3$ is acidified with a weak acid, the reaction practically does not proceed. Only with a great concentration of the hydrogen ions is the formation of hydrogen bromide possible according to the reaction

$$3As_2O_3 + 2HBrO_3 = 3As_2O_5 + 2HBr \qquad \text{(a)}$$

First a very small amount of hydrogen bromide is formed, but then the reaction of oxidation of arsenic trioxide by bromic acid proceeds with self-acceleration under the influence of the increasing amount of HBr. If at the very beginning of the process the rate of the reaction is very low, it gradually grows and reaches a maximum when half of all the bromic acid is reduced.

The hydrogen bromide causes the following reactions, which lead to the regeneration of HBr:

$$HBrO_3 + HBr \rightarrow HBrO_2 + HBrO \qquad \text{(b)}$$

$$4HBr + HBrO + HBrO_2 \rightarrow 3Br_2 + 3H_2O \qquad \text{(c)}$$

$$2Br_2 + As_2O_3 + 2H_2O \rightarrow As_2O_5 + 4HBr \qquad \text{(d)}$$

The process as a whole is a self-inductive one, since the inductor (HBr) appears in the system as a result of the primary reaction (a) and the main reaction (d). Here the actor is $HBrO_3$, and the acceptor $As_2O_3$.

In reactions (b) and (c) the hydrogen bromide is consumed, and in reaction (d) it is regenerated, so that repetition of reactions (b) and (c) is possible.

As can be seen from the above system of reactions, the formation of six molecules of HBr as a result of the process corresponds to the five molecules of HBr

entering into reaction. Thus the process should proceed with an initial self-acceleration due to an increase in the amount of the intermediate (HBr). The entire process of oxidation of arsenic trioxide [reaction (a)] will proceed according to the three reactions (b), (c) and (d), and very slowly. This reaction can be considered as the reaction of origination of the process, and reactions (b), (c) and (d) as reactions of development of the process.

Reaction (b) proceeds slowly, but more rapidly than reaction (a) and determines the rate of the process as a whole, while reactions (c) and (d) proceed quite rapidly. Thus under the action of the inductor (HBr), which is a weak oxidizer, more powerful oxidizers are formed, which conduct the process of oxidation very rapidly. This is the difference of principle of conjugated self-inductive processes and, as we shall see later, of chain processes from catalytic and autocatalytic ones. In catalytic and autocatalytic processes there is only one type of accelerator (the catalyst). It is not only a product, but also a reactant, since it is introduced into a reaction from the very beginning. In the course of a self-inductive conjugated process the inductor (in the example considered HBr) is first formed from the reactants, and then causes the appearance of very active chemical products which "instantaneously" enter into the reactions and stimulate such processes that would be impossible without them. It is interesting to note that the molecules of the intermediates HBr, HBrO and $HBrO_2$ are parts of the initial molecule $HBrO_3$. The energy necessary for their appearance is liberated as a result of chemical induction. Since the slow reaction (b) is bimolecular, its rate is proportional to the product of the concentrations of hydrogen bromide and bromic acid. This reaction determines the rate of the process of oxidation of arsenic trioxide and, consequently, the kinetic equation of this process. We can therefore write that

$$\frac{d[As_2O_5]}{dt} = k_1 [HBr] [HBrO_3] \tag{7.11}$$

Let us denote the initial concentration of $HBrO_3$ by $c_0$, and the reduced concentration, i.e. the amount of hydrogen bromide formed, by $c$. The concentration of the arsenic pentoxide formed will obviously be proportional to the concentration of the hydrogen bromide formed, i.e.

$$\frac{d[As_2O_5]}{dt} = a \frac{d[HBr]}{dt} \tag{7.11a}$$

where $a$ is a proportionality factor.

Equation (7.11) can therefore be rewritten in the form

$$k_1 = \frac{dc}{dt} = kc(c_0 - c) \tag{7.12}$$

where $k \neq k_1$ (owing to the inclusion of a proportionality factor in the quantity $k$).

With the aid of this expression it is easy to determine at what concentration of the bromic acid which has reacted the rate of the reaction will be maximum. Differentiating Eq. (7.12) with respect to the concentration and equating the derivative to zero, we get

$$c = c_0/2 \tag{7.13}$$

which corresponds to the experimental data obtained by Shilov.

Equation (7.12) is an approximate one. It does not describe the initial steps of the process, since if $c = 0$, the process in general cannot start. The constant $k$ in this equation does not have the physical meaning which it has in the ordinary kinetic formulas. It does not reflect the initial rate of the process at $c_0 = 1$. This is explained by the fact that in deducing Eq. (7.12) no account was taken of reaction (a) that resulted in the formation of an intermediate product (HBr) and that caused development of the process [reactions (b), (c) and (d)].

If we take into account that the process can begin only when a certain, though very small, amount of the inductor is formed in the system or, which is the same, when a "seed" in the form of HBr is introduced into the system, then designating this small concentration of HBr by $c_0'$, Eq. (7.12) can be written as

$$\frac{dc}{dt}=k\,(c_0'+c)\,(c_0-c) \tag{7.14}$$

Integration of this equation yields

$$k=\frac{1}{t\,(c_0'+c_0)}\ln\frac{c_0'+c}{b\,(c_0-c)} \tag{7.15}$$

where $b = c_0'/c_0$.

If $c \gg c_0'$ and $c_0 \gg c$, then neglecting the small quantities, we have

$$k=\frac{1}{tc_0}\ln\frac{c}{c_0 b} \tag{7.16}$$

whence

$$c=\alpha e^{t/\tau} \tag{7.17}$$

where $\tau = 1/kc_0$ and $\alpha = c_0 b$.

It follows from this approximate expression that when $t = \tau$ the amount of product increases $e$ times.

Conjugated reactions are widespread in nature. We encounter simultaneously proceeding chemical processes very frequently, especially in biochemistry, and only in rare instances do they proceed independently. It is very difficult, however, to detect the reactive intermediates appearing in the course of a process, and for this reason the mechanism of conjugated reactions has meanwhile been studied insufficiently. The general theory of conjugated processes developed by Shilov can also be extended to the description of processes which at present have been named *chain* ones.

# CHAPTER 8

# CHAIN REACTIONS

**8.1. General. Examples of Chain Reactions.** It has been established experimentally that in a whole series of chemical reactions active particles are first formed in the system. These are most frequently free atoms and radicals that have free valences and are therefore very reactive. These particles enter into a reaction, but again free atoms and radicals are formed. Such a periodically repeating sequence of reactions is called a *chain reaction.*

Thus, the birth of a very small number of such reactive particles leads to the transformation of a great amount of the reactants. Chain reactions are generally of a *cyclic* nature. An active particle regenerated at the end of a cycle begins a new cycle, at the end of which an active particle is again regenerated.

Notwithstanding the fact that the process of formation of a free atom or radical requires a great expenditure of energy, the easiness of interaction of free radicals with saturated molecules and the regeneration of new free radicals leads to the fact that the rate of a chain process may be greater than that of a non-chain one. This can explain the great number of chemical chain reactions.

A typical example of a chain reaction is the reaction of combination of chlorine with hydrogen in light. If a mixture of gaseous chlorine and hydrogen is illuminated for a very short time (for example, with a spark), an explosion reaction of formation of hydrogen chloride will occur. This is explained by the fact that after the elementary photochemical act consisting, as has been proved experimentally, in the decomposition into atoms of a molecule of chlorine which has absorbed light, the products of this primary reaction—the chlorine atoms—and the products of the secondary reaction—the hydrogen atoms—enter into a long chain of reactions with the molecules of chlorine and hydrogen that have not absorbed light. This reaction, whose scheme was proposed by W. Nernst, can be written as follows:

$$Cl_2 \xrightarrow{+h\nu} 2Cl \qquad \text{Initiation of chain}^{1} \qquad \text{(I)}$$

$$\left.\begin{array}{l} Cl + H_2 \longrightarrow HCl + H \\ H + Cl_2 \longrightarrow HCl + Cl \end{array}\right\} \text{Propagation of chain} \qquad \text{(II)}$$

. . . . . .

$$\left.\begin{array}{l} 2Cl \longrightarrow Cl_2 \\ 2H \longrightarrow H_2 \end{array}\right\} \text{Breaking of chain} \qquad \text{(III)}$$

[1] This reaction can proceed not only under the action of light, but also as a result of other causes, for example under the action of thermal motion.

Three groups of reactions can be separated in this scheme. The first one includes the primary reaction of dissociation of chlorine under the action of light—a *chain initiation reaction*. A feature of reaction (I) is that it results in the formation of active centres—chlorine atoms. It should be noted that free atoms, as in the reaction being considered, radicals or chemically active molecules having an excess of internal energy may serve as the active centres.

The atomic chlorine produced can react with molecular hydrogen to form atomic hydrogen. The latter, in turn, can react with molecular chlorine to form atomic chlorine.

Thus, reaction (I) initiates consecutive cycles—the chain reaction develops (*chain propagation*):

$$Cl \rightarrow H \rightarrow Cl \rightarrow H \rightarrow Cl \rightarrow \ldots$$

Reactions of the third group leading to destruction of the active particles, or when they are sufficiently intensive to discontinuation of the chain reaction, are called *chain breaking reactions*. The number of cycles from the moment of initiation of a chain to its breaking is called the *length of the chain*.

It is general knowledge that the recombination of atoms as a bimolecular process is impossible in a bulk, since the energy liberated upon the formation of a molecule is sufficient for breaking the bond that appears. For stabilization of the molecule formed, the presence of a third particle which would take up the excess energy is essential. The role of such a third particle can be played by a molecule of a foreign substance or the wall of the reaction vessel.

At low pressures the active centres are destroyed on the walls, at high pressures trimolecular breaking occurs. For example:

$$Cl + Cl + M \rightleftharpoons Cl_2 + M$$
$$H + H + M \rightleftharpoons H_2 + M$$

(where M is the third particle). In the presence of oxygen the chain breaks as a result of the reaction

$$H + O_2 + M \rightleftharpoons HO_2^{\cdot} + M$$

with the following destruction of the $HO_2^{\cdot}$ on the walls or according to the reaction

$$HO_2^{\cdot} + H \rightleftharpoons H_2 + O_2$$

Similar processes are possible for chlorine atoms. Therefore characteristic of chain reactions is the dependence of the reaction rate on the specific surface area (the ratio of the surface area of a vessel to its volume) of the reaction vessel, on the presence of an inert substance and on the pressure or concentration of the reactants. The reaction proceeds as an explosive one only when definite values

of the pressure are reached. The dependence of the rate of a reaction on the diameter of the vessel and on the addition of inert gases serves as an indication of a chain reaction, but this feature is not essential. For example, in chain reactions in which the chains initiate and break on the walls such a dependence may not exist.

Chain processes should be distinguished from catalytic and autocatalytic ones, although the propagation of the latter also has a cyclic nature. One of the main differences of catalytic reactions from chain ones is the absence of the chain initiation reaction, since one of the intermediates C is present among the reactants and is called a *catalyst*. In addition, chain breaking reactions are characteristic of chain reactions. A feature of chain reactions is also the fact that one reaction in them, proceeding spontaneously with a reduction in the free energy, may initiate other reactions proceeding with an increase in the free energy.

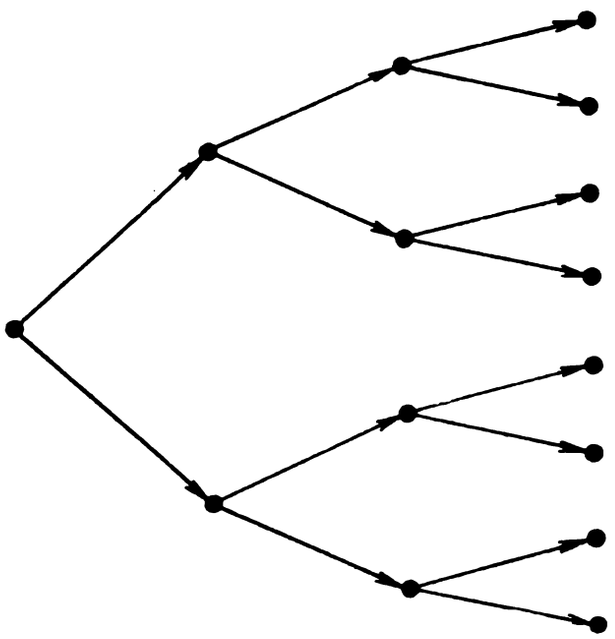


Fig. 8.1. Diagram of a branching chain process

If a single elementary act results in the appearance of two or more chemically active particles, such a process is called a *branching chain* one. The number of active centres and, consequently, the rate of the process in the initial period of time will grow like an avalanche until the moment when as a result of consumption of the reactant the rate of the process begins to decrease.

The reactions of combustion of hydrocarbons can serve as an example of such processes. For instance, in the oxidation of methane there may occur a reaction between the radical $HO_2\cdot$, which appears at sufficiently high temperatures, one of the primary products of oxidation—formaldehyde—and oxygen with the formation of three radicals of $^{\cdot}OH$ according to the equation

$$HO_2^{\cdot} + HCOH + O_2 \rightarrow CO_2 + 3HO^{\cdot}$$

If every elementary act leads to branching of a chain, a reaction with greatly branching chains occurs. An example of such a reaction is that of oxidation of hydrogen at low pressures and at temperatures of about 900 °C. One elementary act results in the appearance of two radicals, and in certain reactions—of atoms of oxygen with two unsaturated valences (—O—) that enter into reaction with a hydrogen molecule and give birth to two free radicals. Such a reaction is

shown schematically in Fig. 8.1. Here we consider the atoms as a particular case of free radicals. The chain initiation reactions for this reaction are as follows:

$$H + O_2 \rightarrow OH\cdot + O$$
$$O + H_2 \rightarrow OH\cdot + H$$
$$OH\cdot + H_2 \rightarrow H_2O + H$$

If branching does not occur during every elementary act of a reaction, but only seldomly, reactions with a sparsely branching chain are observed. Such a reaction is shown schematically in Fig. 8.2, and an example is the reaction of oxidation of hydrogen at high pressures and a temperature of about 500 °C, in which the following processes proceed:

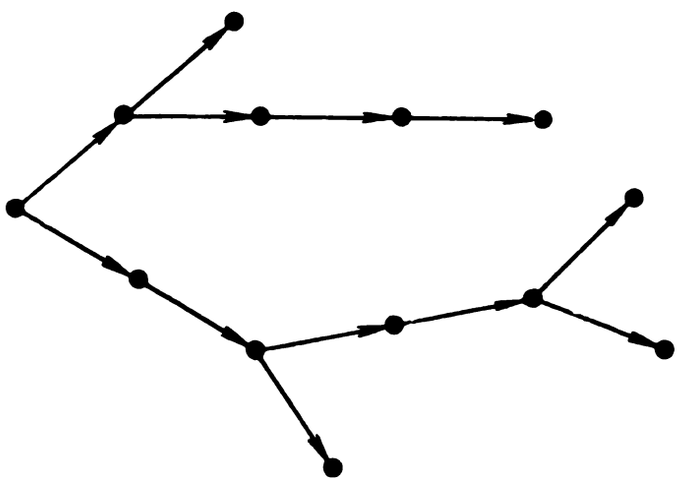


Fig. 8.2. Diagram of a reaction with a sparsely branching chain

$$H + O_2 + M \longrightarrow HO_2\cdot + M$$
$$HO_2\cdot + H_2 \longrightarrow H_2O_2 + H \text{ etc.}$$
$$H + O_2 \longrightarrow OH\cdot + O$$
$$OH\cdot + H_2 \longrightarrow H_2O + H$$
$$O + H_2 \longrightarrow OH\cdot + H$$

In these conditions the reaction $H + O_2 \rightarrow OH\cdot + O$ proceeds at a slower rate than the reaction $H + O_2 + M \rightarrow HO_2\cdot + M$, which leads to sparse branching, since the last reaction at high pressures proceeds more rapidly than the first endothermic reaction.

Sometimes reactions become branching ones owing to the formation of lowly stable molecules of the product, which decompose with the formation of free radicals. Such reactions are sometimes called *reactions with degenerated branching*. Here the branching is always sparse. An example is the reaction of oxidation of methane proceeding according to the scheme

$$CH_3\cdot + O_2 \longrightarrow CH_3OO\cdot$$
$$CH_3OO\cdot + CH_4 \longrightarrow CH_3OOH + CH_3\cdot \text{ etc.}$$

There is a small probability that the peroxide produced will decompose and form free radicals, which results in the so-called degenerated branching proceeding as follows:

$$CH_3OOH \longrightarrow CH_3O\cdot + OH\cdot$$
$$CH_3O\cdot + CH_4 \longrightarrow CH_3OH + CH_3\cdot$$
$$OH\cdot + CH_4 \longrightarrow CH_3\cdot + H_2O$$

The peroxide may also decompose in a different way, for example

$$CH_3OOH \longrightarrow CH_2O + H_2O$$

If as a result of a chain initiating reaction a free radical or atom with one free valence is formed, the chain will be an unbranching one (for example, the reaction of chlorine with hydrogen).

Any reaction may proceed either by simple regrouping of the bonds or as a chain one with the formation and participation of free atoms and radicals in the process. As already indicated above, radi-

cals have a high reactivity and, in addition, in the reaction of a monovalent free radical with a molecule, the free valence is not destroyed, which facilitates propagation of the chain.

For example, the reaction of decomposition of acetaldehyde conducted in the gaseous phase at a temperature of about 500 °C may proceed either as a reaction of direct decomposition of each separate molecule with the formation of methane and carbon monoxide

$$CH_3CHO \rightarrow CH_4 + CO$$

or as a chain reaction with the formation of free radicals

$$CH_3CHO \longrightarrow CH_3\cdot + HCO\cdot \quad \text{Chain initiation}$$

$$\left.\begin{aligned} CH_3\cdot + CH_3CHO &\longrightarrow CH_4 + CH_3CO\cdot \\ CH_3CO\cdot &\longrightarrow CH_3\cdot + CO \text{ etc.} \end{aligned}\right\} \text{Chain propagation}$$

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6 \quad \text{Chain breaking}$$

The mechanism of this reaction has been studied insufficiently, but experience shows that the reaction proceeds like a chain one. Notwithstanding the very slow initiation of the chain, the rate of a chain reaction is found to be many times greater than that of a simple reaction.

Another example showing the possibility of a molecular or a chain mechanism of a reaction is the reaction of formation of hydrogen halides. As we have seen above, the reaction of formation of hydrogen chloride from molecular chlorine and hydrogen proceeds as a typical chain reaction. For the reaction of bromine with hydrogen

$$Br + H_2 \rightarrow HBr + H; \ \Delta H = 15 \text{ kcal/mol}$$

the length of the chains, owing to the endothermic nature of the reaction, is much smaller than in the reaction of chlorine with hydrogen. The mechanism of the reaction of iodine with hydrogen is molecular, and this reaction is a typical bimolecular one, which is the result of its high endothermicity:

$$I + H_2 \rightarrow HI + H; \ \Delta H = 33 \text{ kcal/mol}$$

The iodine atoms formed recombine into molecules without having time to react with the molecular hydrogen.

Many processes of oxidation and combustion, cracking, polymerization, halogenation, etc. are chain ones. Experiments show that when hydrocarbon vapours are heated, especially at a low pressure (of the order of 1-2 mm Hg and less), free radicals are formed. For this reason the kinetics of hydrocarbon cracking was explained on the basis of a chain mechanism of the process with the participation of free radicals. Although to date direct data are not available for judging on the elementary processes that proceed in the thermal cracking of hydrocarbons, we can nevertheless propose such schemes

of reactions with the participation of free radicals which agree with experimental data. For example, in the cracking of propane, the first steps of the process may be as follows:

$$C_3H_8 \longrightarrow C_2H_5\cdot + CH_3\cdot$$
$$C_2H_5\cdot \longrightarrow CH_2{=}CH_2 + H$$

Next reactions proceed with the participation of a methyl radical

$$C_3H_8 + CH_3\cdot \longrightarrow CH_4 + C_3H_7\cdot$$
$$C_3H_7\cdot \longrightarrow CH_2{=}CH_2 + CH_3\cdot \text{ etc.}$$

and reactions with the participation of atomic hydrogen

$$C_3H_7\cdot + H \longrightarrow H_2 + CH_3\dot{C}HCH_3$$
$$CH_3\dot{C}HCH_3 \longrightarrow CH_3CH{=}CH_2 + H \text{ etc.}$$

A variety of other processes may also be assumed. But already the scheme of the course of the reaction given above shows the proper relation between the amount of hydrogen, propylene, methane and ethylene that are the products of the thermal cracking of propane. If we assume that the probability of bond breaking is $e^{-E/RT}$ (where $E$ is the bond energy), then calculations show that the products of decomposition of propane at 650°C should contain 19.5% of hydrogen, 20.5% of methane and 40% of ethylene and propylene (their sum). Experimental data show the formation of 21-22% of hydrogen, 28-31% of methane and 47-50% of ethylene and propylene. It can be seen that the calculated data coincide quite closely with the experimental ones. Notwithstanding the high endothermicity of the process of formation of free radicals, which approximately corresponds to the energy of breaking of the corresponding bond, i.e. has the order of tens of kcal/mol, the relative easiness of carrying out the intermediate steps makes a chain process considerably more advantageous than simple monomolecular decomposition according to the reactions

$$C_3H_8 \rightarrow C_3H_6 + H_2$$
$$C_3H_8 \rightarrow CH_4 + C_2H_4$$

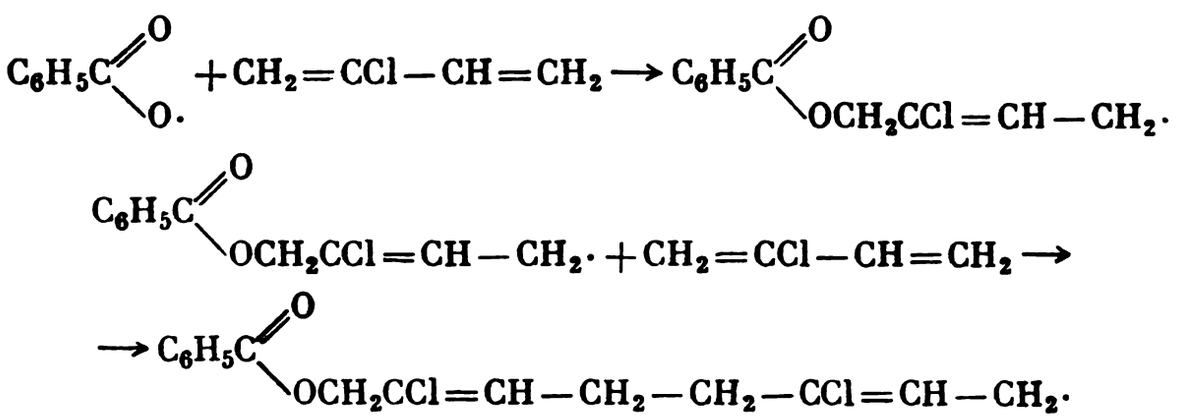
It is interesting to note (this will be shown in detail below) that the chain reaction of thermal decomposition of hydrocarbons is often described by a kinetic equation of a first-order reaction.

Reactions of polymerization, which are of a great practical significance, very frequently proceed with the participation of free radicals. Such polymerization has been called *radical*. The initiation of chains associated with the formation of free radicals may occur under the action of light, $\gamma$-radiation, $\beta$- or $\alpha$-particles, neutrons, an electric discharge, heating (*thermal polymerization*), or under the influence of initiators (*initiated polymerization*). If initiators are

used, the capacity of which is most frequently filled by peroxides, free radicals are formed as a result of dissociation of the initiator molecules. The group of initiators includes benzoyl peroxide, tetralin peroxide, hydrogen peroxide, ammonium persulphate, diazoamino benzene, hexaphenyl ethane, and tetraphenylamber acid dinitrile. The free radicals appear as a result of decomposition of the original initiator, as can be seen on the example of benzoyl peroxide or hexaphenyl ethane:

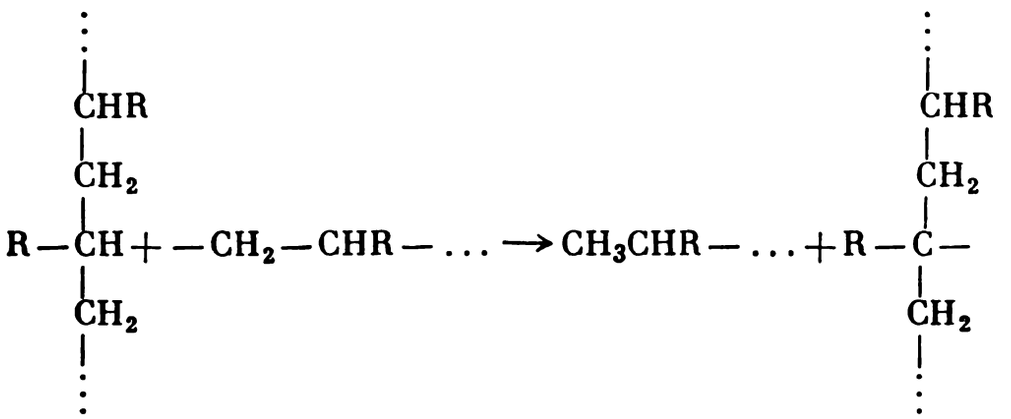
$$(C_6H_5COO)_2 \longrightarrow C_6H_5\cdot + CO_2 + C_6H_5COO\cdot$$
$$(C_6H_5)_3C-C(C_6H_5)_3 \longrightarrow 2(C_6H_5)_3C\cdot$$

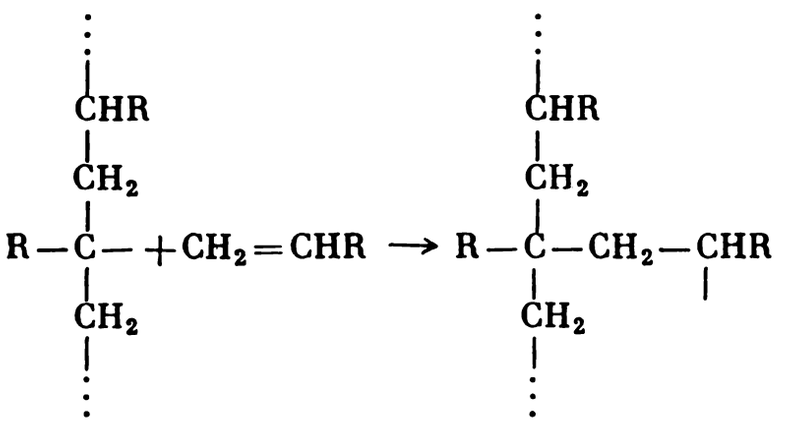
The free radicals formed, combining with a monomer, transform it into a more complex free radical. For example, the polymerization of chloroprene under the action of benzoyl peroxide proceeds as follows:



Thus, free radicals appearing upon the decomposition of the initiator enter the composition of the polymer molecule in the form of terminal groups. As follows from the above scheme, such chains have a material nature, since each link of the chain reaction increases the length of the polymer chain. In this case the length of the chain (the number of cycles) is equal to the number of monomer molecules in a polymer one. Breaking of the material chains leads to completion of the process of macromolecule formation. The chains may be broken as a result of a collision of a reacting chain with a radical, owing to which the free valences become saturated. The collision of radicals may lead to chain breaking owing to the transition of a hydrogen atom from one reacting chain to another, as a result of which the growth of both molecules stops, since a double bond appears in one of them, and the other becomes saturated. A chain may be broken as a result of a collision of a growing radical with molecules of the solvent, monomer or polymer, which leads to saturation of the free valence of the given radical and to the formation of a new free radical initiating a new chain of reactions. This process is called *chain transfer*. A chain transfer process may lead to branching of the material chains and to the formation of so-called *three-dimensional polymers* according to the following sche-

me, in which R denotes a radical, the dots show the continuation of the chain of radicals with saturated valences in the molecule of the polymer, and the dash indicates a free valence:





Quite a great number of chain reactions are known that can be initiated by the addition of a small amount of substances facilitating the formation of free radicals, or as a result of decomposition of these substances which themselves form free radicals (for example, peroxides in polymerization), or as a result of chemical reactions of the initiator with the reactants (for example, acceleration of the reaction between chlorine and hydrogen in the dark in the presence of sodium vapour; the sodium atoms react with the molecular chlorine to form saturated molecules of sodium chloride and chlorine atoms according to the reaction $Na + Cl_2 \rightarrow NaCl + Cl$).

Many reactions of oxidation of hydrocarbons proceed like chain ones with degenerated branches, and for this reason they are frequently associated with great induction periods, when the rate of the reaction is immeasurably small. In the liquid phase (for instance, in the oxidation of paraffin) the induction periods sometimes reach hundreds of hours. When a small amount of nitrogen oxides is added to a mixture, the induction period diminishes owing to the more rapid generation of radicals as a result of reaction of the nitrogen oxides with the hydrocarbons. It is sufficient to add the nitrogen oxides only at the beginning of the reaction which then develops independently.

The generation of radicals, as will be shown below, can also be caused by radiation of various types. Reactions initiated by the addition of substances or the action of radiation facilitating the formation of radicals in the system are called *induced chain reactions.*

The appearance of radicals does not always cause the initiation of a chain chemical process. Everything depends on the reactivity of the radicals formed and on the heat of the reaction which the radical is participating in. For example, when oxygen is added to a mixture of chlorine and hydrogen, the chains break. In the presence of oxygen, as has already been indicated, the hydrogen atoms enter into the reaction

$$H + O_2 + M \rightarrow HO_2^{\cdot} + M$$

(where M is any particle), forming a low-activity radical $HO_2^{\cdot}$ that is not capable of continuing the chain. The radicals $HO_2^{\cdot}$ recombine in the bulk or on the walls.

Another example of a radical with a low activity is the allyl radical $CH_2{=}CH{-}CH_2\cdot$ in which the free valence is conjugated with a double bond. The addition of propylene to a mixture of hydrocarbons participating in chain reactions leads to breaking of the chains, since the propylene reacts with the active radical and transforms into the inert radical $CH_2{=}CH{-}CH_2^{\cdot}$ . A similar radical with a low activity is $NO\cdot$.

A radical may also have a low activity if the reaction which it enters into is appreciably endothermic. An example is the iodine atom in the reaction $H_2 + I$ which, as already noted above, proceeds as a bimolecular one.

The phenomenon of *negative catalysis* by substances combining with the active carriers of the reaction, which leads to breaking of the chains, frequently occurs in chain reactions. For example, in the decomposition of hydrocarbons, radicals like methyl $CH_3\cdot$ that can react with nitrogen oxide according to the equation

$$CH_3\cdot + NO \rightarrow H_2O + HCN$$

are active particles. This reaction leads to breaking of the chains and inhibition of the decomposition reactions, which reduces the overall rate of the reaction scores of times.

The reactions of oxidation of liquid hydrocarbons are inhibited by phenol, amines and other substances, called *inhibitors.*

The reactions of fission of the nuclei of $^{235}U$, $^{239}Pu$ and $^{233}U$ are chain ones. In the process of fission of a nucleus of uranium or plutonium caused by the capture of a neutron, two or three neutrons are emitted. The latter are captured by other nuclei of uranium or plutonium, which in certain conditions leads to their fission. Every neutron can induce the fission of one nucleus of uranium or plutonium. Consequently, the number of neutrons produced in fission grows

in a geometrical progression. Thus, if the predominant number of fission neutrons can cause new fission acts, an avalanche-like growth of the number of disintegrating atoms is observed and, consequently, of the number of neutrons and the amount of energy liberated, i.e. a typical branching process takes place in which the neutrons play the part of the intermediate. It is this process which is used in the production of atomic energy.

**8.2. Length of Chain and Length of Branch.** The concepts *length of chain* and *length of branch* are of great importance for characterizing chain processes. The length of a chain, as indicated above, is equal to the number of reactions (cycles) appearing as a result of the first entering into the reaction of one molecule of the intermediate. Most frequently the latter is represented by atoms or radicals, which should be considered as molecules of a special kind. The entering of one molecule of the intermediate into the first reaction (or into the first cycle) gives on the average $\omega$ new molecules of the intermediate. Entering again into the reaction, they give $\omega^2$ molecules of the same product, etc. For simple unbranching chain reactions the value of $\omega$ may be only less than or equal to unity, since the quantity $\omega$ is simultaneously the probability of the fact that the unbranching chain does not break at the given step, but forms a new active molecule that begins a new step.

Thus the total number of reactions, i.e. the length of a chain, is

$$L = 1 + \omega + \omega^2 + \omega^3 + \ldots = \frac{1}{1-\omega} \tag{8.1}$$

If $\omega = 1$, then the entering of one active particle into a reaction leads to the generation of one active particle. Here the length of the chain, as can be seen from Eq. (8.1), is equal to infinity, and the process is a stationary one. If $\omega < 1$, then the process will obviously be an attenuating one and the length of the chain $L$, as can be seen from Eq. (8.1), will be greater than unity ($L > 1$).

The chain length can also be determined as the ratio between the rate of formation of the product and the rate of reduction of the number of active particles. It is easy to see that this definition does not contradict the one given above. Indeed, let $\Delta a$ molecules of the product be formed during the interval of time $\Delta t$, and $\Delta n$ be the reduction in the number of molecules of the intermediate. According to the last definition, the length of a chain

$$L = \frac{\Delta a}{\Delta n} \tag{8.2}$$

If the process is a chain one, then at least partial regeneration of the intermediate takes place, i.e.

$$\Delta n = \Delta n' - \Delta n'' \tag{8.3}$$

where $\Delta n$ = observed reduction in number of molecules of intermediate

$\Delta n'$ = primary reduction in number of molecules of the intermediate

$\Delta n''$ = number of regenerated molecules of intermediate.

Inserting Eq. (8.3) into Eq. (8.2), we get

$$L = \frac{\Delta a}{\Delta n' - \Delta n''} \tag{8.4}$$

Let us divide the numerator and denominator of Eq. (8.4) by $\Delta n'$. Here

$$\frac{\Delta a}{\Delta n'} = 1 \tag{8.5}$$

since most frequently one molecule of the product corresponds to one destroyed molecule of the intermediate. The ratio

$$\frac{\Delta n''}{\Delta n'} = \omega \tag{8.6}$$

shows the number of molecules of the intermediate forming as a result of the destroying of one of its molecules. Inserting Eqs. (8.5) and (8.6) into Eq. (8.4), we get the previously deduced equation (8.1).

As we have seen above, there are chain reactions in which the destroying of one active particle leads to the appearance of a great number of such particles. These are the so-called *branching chain processes*. For them $\omega > 1$ and, consequently, Eq. (8.1) cannot be applied to them. Equation (8.4) can be used, however, since when $\Delta n'' > \Delta n'$ the value of $L$ is less than zero. Negative values of $L$ have no physical meaning, but they indicate a branching chain process proceeding with self-acceleration.

If $\omega > 1$, the absolute value of the quantity $L$

$$|L| = \frac{1}{\omega - 1} \tag{8.7}$$

shows not the length of the chain, but that of a branch, i.e. the number of primary elementary reactions $\mu$ that will take place up to the moment of branching, when the amount of the active product increases by one particle. This is confirmed by Eq. (8.4). Writing the absolute value of $L$ as

$$|L| = \frac{\Delta a}{\Delta n'' - \Delta n'} \tag{8.8}$$

we see that when $\Delta n'' - \Delta n' = 1$, we have

$$|L| = \Delta a \tag{8.9}$$

i.e. the value of $|L|$ corresponds to the number of molecules of the product formed by the moment of branching, when one particle of

the intermediate appears. In the general case in branching processes, except for reactions in which two or more molecules of the intermediate form instead of one molecule entering into the reaction, there are cases of simple regeneration, when only one molecule of the intermediate is regenerated instead of one molecule entering into the reaction. The length of a branch shows how many simple regenerations occur on the average between two branchings. The more frequently branchings are encountered, the shorter is the length of a branch. With a completely branching chain $\omega = 2$, and the length of a branch becomes equal to unity.

**8.3. Kinetics of Unbranching Chain Reactions.** If in Eq. (8.2) the quantities $\Delta a$ and $\Delta n$ are determined for $\Delta t = 1$, then

$$\Delta a = J \tag{8.10}$$

i.e. the rate of the reaction. Inserting Eq. (8.10) into Eq. (8.2), we find that

$$J = L\,\Delta n \tag{8.11}$$

Thus, if we can determine in some way the length of a chain and the number of molecules of the active product formed in a unit of time, we can also easily find the rate of the chemical reaction. All the quantities in the right-hand part of the equation are a function of time. After a certain delay during which initiation of the chains occurs, the reaction proceeds smoothly with a constantly decreasing rate, since a reduction in the concentration of the reactants leads to a reduction in the number of collisions and, consequently, in the values of $L$ and $\Delta n$.

The length of the chain and the number of active particles formed in a unit of time can be found quite easily for simple photochemical reactions. The length of the chain for these reactions is equal to the number of molecules of the products formed related to one absorbed quantum of light, and the number of active particles formed in a unit of time can be determined if we know the number of light quanta absorbed in a unit of time and the equation of the reaction of the primary photochemical process. For instance, for the photochemical synthesis of hydrogen chloride from chlorine and hydrogen considered above, the primary photochemical process of absorption of a light quantum leads to the appearance of two active particles, namely, two chlorine atoms.

The rate of simple chain reactions usually obeys simple kinetic equations, but frequently owing to great values of the chain length the rate constant for such reactions has an anomalously high value.

For calculating reactions of such a type wide use is made of Bodenstein's stationary-state principle. Although the derivation of the kinetic equation does not involve great difficulty, the complica-

ted nature of the calculation consists in that in the overwhelming majority of cases, as already noted, the detailed mechanism of a reaction is not known. There is practically no method of drawing up the scheme of a chain reaction that uniquely satisfies the empirically found kinetic equation of the reaction. Generally a probable scheme is first drawn up, and the equation of the reaction obtained from it is then compared with experimental data. Let us consider several examples of such reactions.

The reaction of formation of phosgene

$$CO + Cl_2 \rightarrow COCl_2 \qquad \text{(a)}$$

proceeds as an unbranching chain reaction. The reaction is reversible, but at low degrees of transformation it proceeds at a rate that is determined approximately by an equation for an irreversible reaction of the form

$$\frac{d[COCl_2]}{dt} = k[CO][Cl_2]^{3/2} \qquad (8.12)$$

This equation can be obtained by assuming the following reaction mechanism. The bimolecular reaction of chlorine dissociation is the primary process of chain initiation, i.e.

$$Cl_2 + M \xrightarrow{k_1} 2Cl + M \qquad \text{(b)}$$

Here M is any particle ($Cl_2$, CO or a foreign gas) upon collision with which energy is transferred sufficient for dissociation of a chlorine molecule. Next the chain propagation reactions proceed:

$$CO + Cl \xrightarrow{k_2} COCl\cdot \qquad \text{(c)}$$

$$COCl\cdot + Cl_2 \xrightarrow{k_3} COCl_2 + Cl \qquad \text{(d)}$$

as a result of which the initially reacted chlorine atoms are regenerated. In addition, the reaction of decomposition of the radical COCl· takes place:

$$COCl\cdot \xrightarrow{k_4} CO + Cl \qquad \text{(e)}$$

as a result of which the concentration of chlorine atoms becomes higher than that of the radicals COCl··. This leads to the fact that the active particles mainly recombine at the expense of the chlorine atoms, the latter recombining as a result of triple collisions:

$$Cl + Cl + M \xrightarrow{k_5} Cl_2 + M \qquad \text{(f)}$$

The rate of phosgene formation, according to reaction (d), can be written as follows:

$$\frac{d[COCl_2]}{dt} = k_3[COCl\cdot][Cl_2] \qquad (8.13)$$

To determine the concentration of the radical COCl· let us write the equations for the rates of formation of atomic chlorine and the radical COCl·:

$$\frac{d[\mathrm{Cl}]}{dt} = k_1[\mathrm{Cl_2}][\mathrm{M}[ + k_3[\mathrm{COCl}\cdot][\mathrm{Cl_2}] + k_4[\mathrm{COCl}\cdot] - $$
$$- k_2[\mathrm{Cl}][\mathrm{CO}] - k_5[\mathrm{Cl}]^2[\mathrm{M}] \tag{8.14}$$

$$\frac{d[\mathrm{COCl}\cdot]}{dt} = k_2[\mathrm{Cl}][\mathrm{CO}] - k_3[\mathrm{COCl}\cdot][\mathrm{Cl_2}] - k_4[\mathrm{COCl}\cdot] \tag{8.15}$$

In a certain time after the process becomes stationary, we can assume, according to Bodenstein's principle, that

$$\frac{d[\mathrm{Cl}]}{dt} = 0 \quad \text{and} \quad \frac{d[\mathrm{COCl}\cdot]}{dt} = 0$$

For this condition summation of Eqs. (8.14) and (8.15) yields

$$k_1[\mathrm{Cl_2}][\mathrm{M}] = k_5[\mathrm{Cl}]^2[\mathrm{M}] \tag{8.16}$$

whence

$$[\mathrm{Cl}] = \sqrt{\frac{k_1}{k_5}[\mathrm{Cl_2}]} \tag{8.17}$$

From Eq. (8.15), with account of the stationary state, we have

$$[\mathrm{COCl}\cdot] = \frac{k_2[\mathrm{Cl}][\mathrm{CO}]}{k_3[\mathrm{Cl_2}] + k_4} \tag{8.18}$$

or, inserting into this equation the concentration of the chlorine atoms from Eq. (8.17), we get

$$[\mathrm{COCl}\cdot] = \frac{k_2[\mathrm{CO}]\sqrt{\frac{k_1}{k_5}[\mathrm{Cl_2}]}}{k_4 + k_3[\mathrm{Cl_2}]} \tag{8.19}$$

Using the value of [COCl·] in Eq. (8.13), we obtain

$$\frac{d[\mathrm{COCl_2}]}{dt} = \frac{k_2k_3[\mathrm{CO}]\sqrt{\frac{k_1}{k_5}[\mathrm{Cl_2}]^3}}{k_4 + k_3[\mathrm{Cl_2}]} \tag{8.20}$$

This equation acquires the form of empirical equation (8.12) given above if

$$k_4 \gg k_3[\mathrm{Cl_2}] \tag{8.21}$$

i.e. if we assume that reaction (e) proceeds many times more rapidly than reaction (f). This assumption is quite justified, since reaction (f) requires an appreciable activation energy and does not proceed upon every collision, while the radical COCl· is comparatively unstable.

The chain length for the reaction of synthesis of phosgene according to the definition and with account of inequality (8.21) is

$$L = \frac{k_3\,[\mathrm{COCl}\cdot][\mathrm{Cl_2}]}{k_1\,[\mathrm{Cl_2}][\mathrm{M}]} = \frac{k_3[\mathrm{COCl}\cdot]}{k_1[\mathrm{M}]} = \frac{k_2k_3}{k_1\sqrt{k_1k_5}}\,\frac{[\mathrm{CO}]\sqrt{[\mathrm{Cl_2}]}}{[\mathrm{M}]} \qquad (8.22)$$

**8.4*. Thermal Cracking of Hydrocarbons.** An interesting chain reaction that is of great practical importance is the reaction of thermal cracking of hydrocarbons. We can base the deduction of the equation of the kinetics of this reaction either on our knowledge of its specific mechanism, i.e. our knowledge of all the elementary processes which the entire process as a whole consists of, or on certain general qualitative considerations agreeing with experimental data. The first path is practically impossible, since except for some reactions in rarefied flames (see Sec. 4.8), the detailed mechanism of the overwhelming majority of chemical reactions is unknown. Therefore only the second path is a practicable one.

The derivation of the kinetic equation for the thermal cracking of hydrocarbons can be approached, as shown by G. Panchenkov and V. Baranov, on the basis of two ideas of the nature of the processes taking place, which lead to the formally identical type of final equation.

In the general form the reaction of thermal cracking, if its kinetics is judged according to the total transformation of the reactant, can be written as follows on the basis of what has been said in Sec. 1.15:

$$\mathrm{A} \rightarrow \nu_1\mathrm{A}_1 + \nu_2\mathrm{A}_2 + \ldots + \nu_n\mathrm{A}_n$$

Let us assume that the slowest step is the reaction between the molecules of the reactants and the radicals appearing in the course of the reaction and having a small mass. The rate of the reaction of thermal cracking will therefore be determined by the equation

$$J = k\,[\mathrm{R}]\,[\mathrm{A}] \qquad (8.23)$$

Here $k$ is the rate constant of the cracking reaction, and [R] and [A] are the concentrations of the radicals and the reactant, respectively.

A different mechanism of the process is not excluded, however. The rate of the process may be determined by the slow reactions of formation of free radicals. If we take into consideration that the free radicals formed are easily destroyed at sufficiently high pressures (at which cracking is conducted), and the rate of radical formation as a result of decomposition of the initial molecules is low owing to the high activation energy of this process ($E \approx 70$ kcal), then the rate of cracking will be determined by the rate of these two processes—that of decomposition of the initial molecules into free radicals and that of interaction of the radicals with the initial molecules, i.e.

$$J_1 = k_1\,[\mathrm{A}] + k_2\,[\mathrm{R}]\,[\mathrm{A}] \qquad (8.24)$$

The concentrations of the radicals in Eqs. (8.23) and (8.24) can be found, by using the stationary-state principle, as a result of considering the processes leading to the formation and destroying of the radicals. The latter may appear as a result of three processes, namely, bimolecular collisions of the initial molecules, monomolecular decomposition of the initial molecules, and their regeneration as a result of a reaction with the initial molecules. Destroying of the radicals is due to their reaction with the reactant molecules and recombination. The first reaction leads to the formation of radicals with a greater molecular mass, which as a result of regeneration of a radical with a smaller molecular mass transform into the products (for example, alkenes if the reactants are alkanes). The second process has a low probability owing to the great concentration of the reactants.

The rate of the reaction of formation of radicals, if the processes of their generation and destroying are taken into account, is equal to

$$J_2 = k_3 [A]^2 + k_1 [A] - k_4 [A] [R] \tag{8.25}$$

where $k_3$ and $k_1$ are the constants of the rates of generation of the radicals as a result of bimolecular collisions and monomolecular decomposition:

$$k_4 = k_5 - k \tag{8.26}$$

Here $k_5$ is the constant of the rate of regeneration of the radicals as a result of their interaction with the reactant, and $k$ is the constant of the rate of their destroying as a result of this reaction.

According to the stationary-state principle, in a certain time after the beginning of the process

$$J_2 = 0 \tag{8.27}$$

When this condition is observed, from Eq. (8.25) we get

$$[R] = \frac{k_3}{k_4} [A] + \frac{k_1}{k_4} \tag{8.28}$$

Inserting Eq. (8.28) into Eq. (8.23) or (8.24), we get

$$J_1 = k' \{1 + k_3' [A]\} [A] \tag{8.29}$$

where $k' = k \frac{k_1}{k_4}$, and $k_3' = \frac{k_3}{k_1}$ [when inserting into Eq. (8.23)], or $k' = k_1 + k_2 \frac{k_1}{k_4}$ and $k_3' = \frac{k_3}{k_1}$ [when inserting into Eq. (8.24)].

It is only possible to answer the question as to which of the equations should be preferred after detailed investigation of the mechanism of thermal cracking. Equation (8.29) is quite adequate for the solution of practical problems.

If the reaction of radical formation as a result of bimolecular collisions of the initial molecules does not play a significant part, i.e. $k_3$ is very small, the first addend in the right-hand part of Eq. (8.28) can be neglected. Hence

$$[R] = \frac{k_1}{k_4} \tag{8.30}$$

Equation (8.29) becomes a kinetic equation of a first-order reaction:

$$J_1 = k' [A] \tag{8.31}$$

This is possible if cracking proceeds at low pressures; experimental data confirm this conclusion.

If we can neglect the reaction of monomolecular decomposition of the initial molecules into radicals, i.e. if $k_1$ is very small, from Eq. (8.28) we get

$$[R] = \frac{k_3}{k_4} [A] \tag{8.32}$$

Here Eq. (8.29) for the rate of thermal cracking becomes a kinetic equation of a second-order reaction:

$$J_1 = k' k_3 [A]^2 \tag{8.33}$$

An equation of this kind is true for thermal cracking at low temperatures.

Experience shows that the kinetics of thermal cracking conducted at pressures from 1 to 50 atm at temperatures of 500-600 °C is sufficiently accurately described by Eq. (8.29).

**8.5. Branching Chain Reactions.** If branching of chains occurs and if the number of new chains formed in a short period of time is greater than the number of breaking chains, the rate of the reaction rapidly grows and an explosion may occur, although the temperature does not grow to such an extent as to make a thermal explosion possible. Experiments show that the transition of a reaction to explosion conditions is possible only at quite definite pressures (or concentrations) and temperatures of the reaction mixture. At a given temperature there exist pressure limits within which an explosion or self-ignition is possible.

Reactions in the course of which self-ignition occurs at definite pressures were known long ago owing to their very peculiar properties. The mechanism of these reactions however was explained comparatively recently,. mainly in the works of N. Semenov and his collaborators. A. Fourcroy back in 1788 discovered that pure oxygen at an ordinary temperature and normal pressure does not react with phosphorus, which in the same conditions is energetically oxidized by air. La Billardiere (1877) found that at atmospheric pressure hydrogen phosphide does not ignite when it comes into contact with air, while at reduced pressures an explosion occurs. These phenomena were later investigated by J. van't Hoff. Similar phenomena were discovered by J. Joubert (1874), who studied the oxidation of arsenic and sulphur, C. Friedel and A. Ladenburg (1871), who investigated the oxidation of silicohydride. The first to pay serious attention to these reactions were Semenov and his collaborators, who again studied the reaction of oxidation of phosphorus by oxygen and established for this reaction the existence of not only an upper, but also a lower limit of self-ignition. Semenov considered processes of such a type as reactions with branching chains. He showed the important part played by deactivation (destroying) of the active particles on the walls and in the bulk, as a result of which the rate of the reaction was found to depend on the dimensions of the vessel. Two explosion limits were established for mixtures with oxygen of such compounds as hydrogen phosphide, sulphur, hydrogen sulphide and carbon disulphide.

The discovery of the lower limit of self-ignition of a mixture of phosphorus with oxygen [Yu. Khariton, Z. Valta and N. Semenov (1926)] served as an impetus to the studying of branching chain reactions. These scientists discovered that the burning of phosphorus vapour in oxygen, which proceeded quite intensively, completely stopped when the partial pressure of the oxygen was reduced to below a certain limiting value equal to about 0.05 mm Hg (the lower critical pressure of self-ignition). A negligible increase in the pressure (by 0.01 mm Hg) was sufficient for ignition to occur once more. At a pressure below the critical one by 0.01 mm Hg the mixture could exist as long as desired. Detailed investigation of this phenomenon showed that the critical partial pressure of oxygen depends on the pressure of the phosphorus vapour, on the diameter of the vessel and on the presence of an inert gas whose addition to the reaction mixture reduces the critical pressure.

The existence of limits of self-ignition and explosiveness was explained after development of the theory of branching chain reac-

tions. This will be considered in detail below, while the phenomenon observed can be qualitatively explained as follows. At low pressures smaller than the lower critical pressure the average number of chain breakings exceeds the number of chain branchings, and combustion becomes impossible.

At pressures above the lower limit, the probability of chain breaking diminishes, since, owing to collisions between the particles, the probability of active particles reaching the walls of the

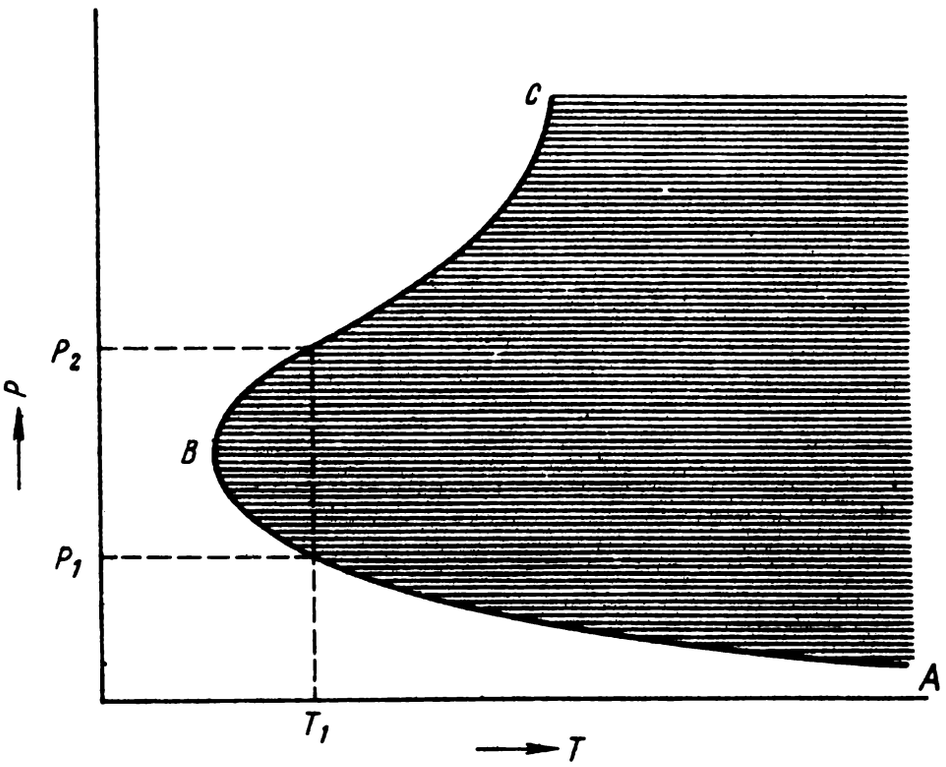



Fig. 8.3. Limits of self-ignition and explosiveness

vessel decreases. The addition of an inert gas and an increase in the diameter of the vessel hamper the diffusion of the active centres to the walls. As a result the rate of the chain breaking reactions decreases, which leads to a reduction of the critical partial pressure of the oxygen at the limit.

As indicated above, upon an increase in the pressure a second critical pressure is observed above which ignition becomes impossible. Here again the average number of chain breakings begins to exceed the number of chain branchings. But now the chains break not on the walls, but in the bulk as a result of triple collisions.

If we plot the temperature dependence of the pressure at which ignition occurs, the curve obtained will frequently have the shape shown in Fig. 8.3. The entire area to the left of curve *ABC* corresponds to conditions in which self-ignition is impossible. The process of self-ignition of a gas mixture is possible only in the hatched area which is called the explosion peninsula. At a certain given temperature $T_1$, as can be seen from the figure, there is a lower pressure limit

$p_1$ below which self-ignition is impossible, and an upper pressure limit $p_2$ above which self-ignition is also impossible.

The value of $p_1$ decreases with a growth in the temperature according to the law $e^{E/RT}$. The value of $p_1$ depends on the diameter of the vessel, the nature of the wall surface, and the composition of the mixture. The quantity $E$ has the order of $10^4$ cal/mol when the yield is low. The position of point $B$, the so-called cape of the explosion peninsula, depends on the same parameters, and it may shift depending on the temperature. The value of $p_2$ grows with an increase in the temperature according to the law $e^{-E_2/RT}$. The value of $E_2$ for the reaction of oxidation of hydrogen is equal to 18 000 cal/mol. The value of $p_2$ depends to a very small extent on the magnitude of the surface area, diameter and the shape of the vessel.

An important characteristic of chain processes is the so-called *induction period*, which, strictly speaking, characterizes the time during which the concentration of the intermediate (the active centtres of the reaction) increases $e$ times. In practice by the induction period is usually meant a conventional quantity—the time during which the rate of a process changes from an insignificant immeasurable value to a very great measurable value. Usually owing to the avalanche-like growth of the rate, the process first develops slowly, but after some time begins to proceed at a great and constantly growing rate.

The pressure dependence of the induction period for the reaction $H_2 + O_2$ at two different concentrations of the oxygen is shown in Fig. 8.4.

The dependence of the induction period on the pressure or concentration of the mixture (at moderate values of $p$) can be described by the approximate equation deduced by N. Akulov:

$$\tau = \frac{\tau_0}{(p - p_1)(p_2 - p)} \qquad (8.34)$$

where $\tau_0$ = constant
$p_1$ and $p_2$ = limits of pressures at which self-ignition occurs.

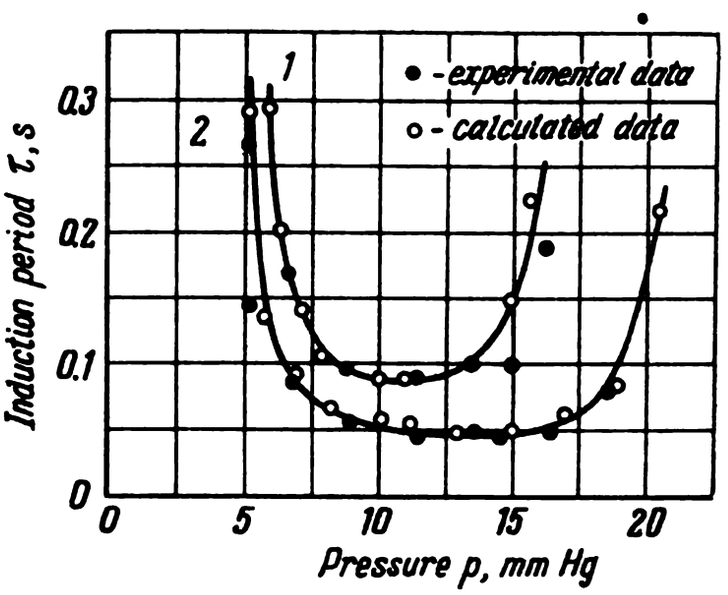



Fig. 8.4. Pressure dependence of induction period for the reaction $H_2 + O_2$ at 442 °C: *1*—mole fraction of $O_2$ equals 0.33; *2*—mole fraction of $O_2$ equals 0.5

It follows from the above equation that when $p < p_1$ or $p > p_2$ the parameter $\tau$ is negative. In this case, as shown by experiments and theory, the process will be an attenuating one ($\omega < 1$ and $L > 0$). In the region $p_1 < p < p_2$ we have $\tau > 0$, and the process will proceed with self-acceleration ($\omega > 1$ and $L < 0$). The induction period becomes equal to infinity at the pressures $p = p_1$ and $p = p_2$. These pressures determine the explosion limits for the reaction. Consequently, the condition of self-ignition limits is equivalent to the condition $\tau = \infty$.

Experiments show that in a number of cases not two, but three ignition or explosion limits are observed. For example, Fig. 8.5 shows the self-ignition limits for the reaction of oxidation of hydrogen sulphide (the theoretical curve and the experimental points are for a vessel radius $R_0 = 4.6$ mm and a mole fraction of $O_2$ equal to 0.6). Branch $AB$ corresponds to the lower (first) limit of self-ignition, branch $BC$ to the upper (second) limit, and $CD$ to the third limit of self-ignition. When the third limit is reached, intensive self-ignition again begins. In most instances the third limit has a purely thermal nature (see Sec. 1.13). Sometimes, in particular in the reaction of oxidation of hydrogen, the third limit has a chain nature, i.e. self-ignition occurs not as a result of acceleration of the reaction due to self-heating, but as a result of the propagation of branching chain reactions. The value of the third pressure limit $p_3$ for the reaction of oxidation of hydrogen grows with a reduction of the temperature according to the law $e^{E_3/RT}$ and depends on the nature of the walls in the same way as the slow reaction below this limit. The position of point $C$ also depends on the nature of the walls.

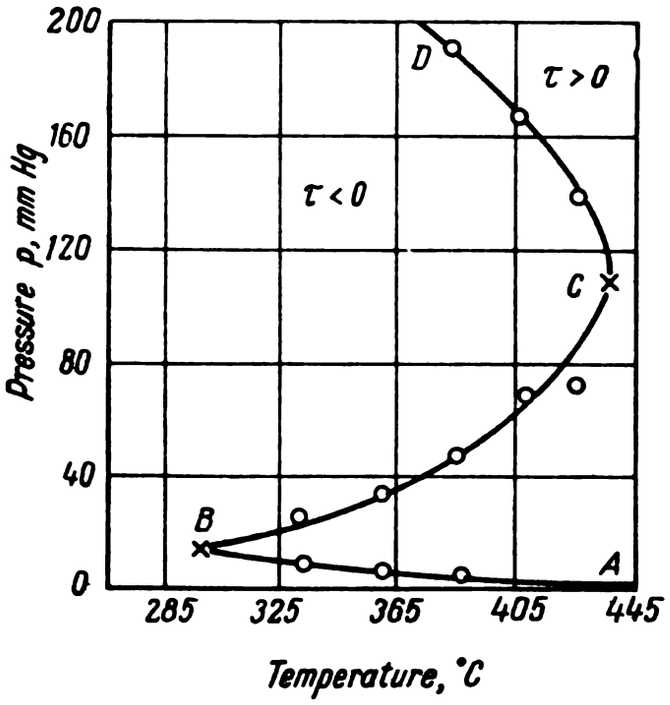



Fig. 8.5. Self-ignition limits for the reaction of oxidation of hydrogen sulphide

It can be shown theoretically (the theory of this problem is quite complicated, and we shall not consider it here) that the third limit can have a chain nature when on the walls of the reaction vessel not only destroying of the free radicals, but also the formation of new free radicals is possible due to the reaction of free radicals with adsorbed molecules. It can also be of a chain nature when at high pressures such triple collisions are possible that lead to the initiation of chains.

It should be noted that the concept *explosion limits* is used in three different meanings. Firstly, the explosion limits are spoken about when the pressure is determined (at a definite temperature) below which a spontaneous explosion cannot occur. In this case the explosion has a purely thermal nature. In an exothermic reaction such a state may set in when the heat removed from a system is less than the heat of the chemical reaction. This will lead to a growth in the temperature of the reaction system and to a sharp growth in the rate of the chemical reaction according to the law $k = ce^{-E/RT}$. Such a thermal autoacceleration of the reaction results in an explosion.

Secondly, the explosion limits should be distinguished that are observed as concentration limits having a chain nature and which have just been considered. In this case two limits of self-ignition are noted, or, in the more general case, as indicated above, three limits of self-ignition and explosion. The third limit of self-ignition may sometimes have a thermal nature.

Thirdly, in technical publications by the upper and lower explosion limits are meant the limiting concentrations when there is an external impulse. It is obvious that outside of the concentration limits, with a foreign source of ignition, an explosion cannot spread through a mixture which is at the given pressure and temperature. When an explosion can occur, its origination in one of the points does not yet mean that it may spread through the entire volume. Here the conditions of propagation of the flame will play an appreciable part. The explosion

originates in a limited space containing the source causing ignition (a spark, a heated wire). Consequently, in this limited space all the conditions (concentration, pressure and temperature) in which a *chain explosion* is possible are observed. But in all the remaining space the temperature is lower than that necessary for accomplishing a chain explosion, and therefore the reactions do not proceed. They can propagate as a result of spreading of the flame from the point of ignition owing to heat transfer from the burning layer to the one bordering with it that is not yet burning, and owing to the growth of pressure caused by burning. It is owing to the increase in the temperature that self-ignition of the layer bordering with the layer of burning gas takes place.

In general, a chain process is possible without the limits of the concentrations, temperatures and pressures essential for self-ignition and explosion, but it will be an attenuating one.

**8.6*. Kinetics of Branching Chain Reactions.** Let us consider the kinetic calculation of branching chain reactions on the example of the sufficiently well investigated reaction of oxidation of hydrogen. This reaction has been considered by many authors. At present, mainly due to B. Lewis, G. von Elbe and N. Semenov, it is considered to consist of the following consecutive elementary chemical processes:

$$\left.\begin{array}{l} H_2+O_2 \longrightarrow 2OH\cdot \\ H_2+M \longrightarrow 2H+M \\ O_2+O_2 \longrightarrow O+O_3 \end{array}\right\} \text{Initiation of chain}$$

$$OH\cdot+H_2 \longrightarrow H_2O+O \quad \text{Propagation}$$

$$\left.\begin{array}{l} H+O_2 \longrightarrow OH\cdot+O \\ O+H_2 \longrightarrow OH\cdot+H \end{array}\right\} \text{Branching}$$

$$\left.\begin{array}{l} H \xrightarrow{\text{wall}} \frac{1}{2}H_2 \\ OH\cdot \xrightarrow{\text{wall}} H_2O_2 \end{array}\right\} \text{Breaking of chains on wall}$$

$$H+O_2+M \longrightarrow HO_2\cdot+M \quad \text{Breaking of chains in bulk}$$

$$HO_2\cdot \xrightarrow{\text{wall}} \left\{\begin{array}{l} \frac{1}{2}H_2O_2+\frac{1}{2}O_2 \\ \frac{1}{2}H_2O+\frac{3}{4}O_2 \end{array}\right.$$

$$\left.\begin{array}{l} HO_2\cdot+H_2 \longrightarrow H_2O_2+H \\ HO_2\cdot+H_2O \longrightarrow H_2O_2+OH\cdot \end{array}\right\} \begin{array}{l}\text{Propagation of chain through} \\ \text{radical with a low activity}\end{array}$$

The formation of atoms of hydrogen and oxygen as a result of the reaction, and also the formation of free hydroxyl were proved by direct experiments; the participation in the reaction of $HO_2\cdot$ radicals with a low activity was proved by indirect experiments. To describe the development of such a complicated process, it is necessary to know the laws of the change with time of the concentrations of all the individual particles in the system. Such a problem is very complicated, and to date it has not yet been solved. For this reason a number of simplifying assumptions have to be used in analysing the kinetics of the process.

A simpler set of elementary reactions is contained in Table 8.1.

In the table the quantity $n_0$ is the concentrations of $H_2$ and $O_2$, $n_1$ is the concentration of atomic oxygen, $n_2$ the concentration of atomic hydrogen, $n_3$ the concentration of the hydroxyl radical. The symbol $A$ denotes the specific surface

area of the reaction vessel. The concentrations of $H_2$, $O_2$ and M—the third particle causing deactivation of the atomic hydrogen—are proportional to the pressure $p$.

TABLE 8.1

**Elementary Branching Chain Reactions**

| Process | Reaction | Activation energy, cal/mol | Expression for rate |
|---|---|---|---|
| Chain initiation | $H_2 + O_2 \rightarrow 2OH\cdot$ | 45 000 | $2k_0n_0^2$ [1] |
| Propagation | $OH\cdot + H_2 \rightarrow H_2O + H$ | $<14\,000$ | $a_3n_3 = k_3pn_3$ |
| Branching | $H + O_2 \rightarrow OH\cdot + O$ | $>20\,000$ | $a_2n_2 = k_2pn_2$ |
| | $O + H_2 \rightarrow OH\cdot + H$ | $<9\,000$ | $a_1n_1 = k_1pn_1$ |
| Chain breaking | $H + O_2 + M \rightarrow HO_2\cdot + M$ | $\approx 0$ | $a_4n_2 = k_4p^2n_2$ |
| | $H \xrightarrow{\text{wall}} \frac{1}{2} H_2$ | $<8\,000$ | $a_5n_2 = k_5An_2$ |

[1] The factor 2 appears because the rate constant relates to the product OH·, and two radicals OH· are obtained for each molecule of $H_2$ (or $O_2$).

In the expressions for the rate constant the designation $a_in_i$ is used, where $n_i$ is the concentration of the active product and $a_i$ is a quantity that determines the rate of the reaction of this product in the given conditions. This quantity at $n_i = 1$ is equal to $k_i$ — the rate constant of the reaction in the given conditions multiplied by the pressure of the initial mixture (at the given composition of the mixture); the pressure is proportional to the concentration of the substance or substances reacting with the active substance to a power corresponding to the stoichiometric equation.

The slowest process determining the rate of the reaction of oxidation of hydrogen is the reaction between the atoms of hydrogen and oxygen, which requires the greatest activation energy. The rate of formation of water (its concentration is designated by $xn_0$) according to the scheme followed will be

$$\frac{dxn_0}{dt} = a_3n_3 = k_3pn_3 \tag{8.35}$$

The hydrogen atoms will accumulate in the system more rapidly than the oxygen ones and the free hydroxyl radicals, and the chain breaking reactions will proceed mainly due to the hydrogen atoms.

The following equations can be written for the rates of formation of atomic oxygen and hydrogen, and of the hydroxyl radical:

$$\frac{dn_1}{dt} = a_2n_2 - a_1n_1 \tag{8.36}$$

$$\frac{dn_2}{dt} = a_3n_3 + a_1n_1 - a_2n_2 - a_4n_2 - a_5n_2 \tag{8.37}$$

$$\frac{dn_3}{dt} = 2k_0n_0^2 + a_1n_1 + a_2n_2 - a_3n_3 \tag{8.38}$$

To simplify calculations we can assume that within a certain interval of time the concentrations of the hydroxyl and the atoms of oxygen become stationa-

ry, i.e.

$$\frac{dn_1}{dt}=\frac{dn_3}{dt}=0 \tag{8.39}$$

Solving the simultaneous equations (8.36)-(8.38) with account taken of Eq. (8.39), we can express all the concentrations of the active particles in terms of the concentrations of atomic hydrogen $n_2$ and of the reactants.

Summation of Eqs. (8.36) and (8.38) yields

$$n_3=\frac{2}{a_3}(k_0n_0^2+a_2n_2) \tag{8.40}$$

Using Eq. (8.40) in Eq. (8.38), we have

$$n_1=\frac{a_2n_2}{a_1} \tag{8.41}$$

Inserting Eqs. (8.40) and (8.41) into Eq. (8.37), we get

$$\frac{dn_2}{dt}=2k_0n_0^2+(2a_2-a_4-a_5)\,n_2 \tag{8.42}$$

or, assuming that

$$2a_2-a_4-a_5=\varphi \tag{8.43}$$

we can write that

$$\frac{dn_2}{dt}=2k_0n_0^2-\varphi n_2 \tag{8.44}$$

The solution of this differential equation will be

$$n_2=\frac{2k_0n_0^2}{\varphi}(e^{\varphi t}-1) \tag{8.45}$$

Insertion of Eq. (8.45) into Eq. (8.40), and of the result into Eq. (8.35) gives

$$\frac{dn_0x}{dt}=a_3n_3=\frac{2k_0n_0^2}{a_3\varphi}(2a_2e^{\varphi t}-2a_2+\varphi) \tag{8.46}$$

Using the expression for the rates of processes (see Table 8.1), we introduce $a_i$ as a function of $p$ into Eq. (8.43). Hence

$$\varphi=2k_2p-k_4p^2-k_5A \tag{8.47}$$

We can write the expression obtained as

$$\varphi=(p-p_1)(p_2-p) \tag{8.48}$$

where $p_1$ and $p_2$ are the roots of the quadratic equation

$$k_4p^2-2k_2p+k_5A=0 \tag{8.49}$$

Solving this quadratic equation, we get

$$p_2=\frac{k_2+\sqrt{k_2^2-4k_4k_5A}}{2k_4} \tag{8.50}$$

$$p_1=\frac{k_2-\sqrt{k_2^2-4k_4k_5A}}{2k_4} \tag{8.51}$$

In the interval of pressures from $p_1$ to $p_2$ the quantity $\varphi$ is positive, and outside of this interval it is negative. At a negative value of $\varphi$ the concentration $n_2$ and, consequently, the rate of the reaction cannot grow rapidly, since in this case, as can be seen from Eq. (8.43), the breaking reactions dominate over the branching ones.

When $\varphi = 0$ the solution of Eq. (8.44) gives

$$n_2 = 2k_0 n_0^2 t \tag{8.52}$$

and Eq. (8.49) upon insertion of Eq. (8.40) into it and with account to Eq. (8.52) becomes

$$\frac{dn_0 x}{dt} = 2k_0 n_0^2 (1 + 2a_2 t) \tag{8.53}$$

A glance at Eq. (8.53) shows that the reaction becomes self-accelerating. The condition that $\varphi = 0$, consequently, is the condition of changing of the reaction from a slow one to a self-accelerating one. In the region $\varphi > 0$ the reaction will proceed as a self-accelerating one, the self-acceleration being the greater, the higher is the value of $\varphi$. In this case the chain branching reactions dominate over the breaking ones.

It follows from Eq. (8.53) that the limits of the pressures $p_1$ and $p_2$ at which the reaction becomes a self-accelerating one depend on the temperature, since the chain branching rate constant $k_2$ depends on the temperature according to the exponential law

$$k_2 = ke^{-E/RT} \tag{8.54}$$

These equations approximately describe experimental data only at low pressures. In the region of high pressures a third limit can be reached which does not follow from the theory considered above. At high pressures account must be taken of the chain propagation reactions carried by $HO_2\cdot$, and also the possibility of the formation of active particles on the walls of the reaction vessel.

The derivation of the kinetics of the process considered above is approximate not only because we simplified the scheme of the process, but also because we used the *method of quasi-stationary concentrations*, which for the case under consideration has not been sufficiently substantiated. A stricter solution of the problem can be obtained by considering the solution of the simultaneous differential equations (8.36), (8.37) and (8.38) in the general form. Such a solution is possible, but the calculations are very cumbersome.

Using Eqs. (8.36) and (8.37) and the principle of stationary conditions, we can obtain an equation describing the kinetics of the process with account taken of burning out of the reactants.

Inserting Eq. (8.40) into Eq. (8.35), we get

$$\frac{dn_0 x}{dt} = 2(k_0 n_0^2 + a_2 n_2) \tag{8.55}$$

To simplify calculations let us consider reactions at low pressures, when $p \approx p_1$. Here the rate of the reaction $H + O_2 + M \rightarrow HO_2\cdot + M$ may be neglected and, consequently, Eq. (8.42) can be written as

$$\frac{dn_2}{dt} = 2k_0 n_0^2 + (2a_2 - a_5)\, n_2 \tag{8.56}$$

Neglecting because of its low value the addend that determines the rate of chain initiation and replacing the pressure with a quantity proportional to it—the concentration of the oxygen, Eqs. (8.55) and (8.56) can be written as

$$\frac{d[O_2]}{dt} = k_2'[O_2][H] \tag{8.57}$$

and

$$\frac{d[H]}{dt} = \{k_2'[O_2] - k_5 A\}[H] \tag{8.58}$$

Dividing Eq. (8.58) by Eq. (8.57), we get

$$-\frac{d[H]}{d[O_2]}=\frac{k_2'[O_2]-k_5A}{k_2'[O_2]} \tag{8.59}$$

In integrating this expression we shall take into account that at the initial concentration of oxygen $[O_2] = [O_2]_0$ the concentration of atomic hydrogen is practically equal to zero ($[H]_0 \approx 0$). From Eq. (8.59) we get

$$[H]=[O_2]_0-[O_2]+\frac{k_5A}{k_2}\ln\frac{[O_2]}{[O_2]_0} \tag{8.60}$$

Inserting this equation into Eq. (8.57), we get

$$-\frac{d[O_2]}{dt}=k_2'[O_2]\left\{[O_2]_0-[O_2]+\frac{k_5A}{k_2}\ln\frac{[O_2]}{[O_2]_0}\right\} \tag{8.61}$$

According to this equation the rate of the reaction first grows, next passes through a maximum near half of the total transformation and then reduces toward the end of the reaction. It already follows from the derivation of this equation that it has an approximate nature and holds only within a certain interval of time.

The modern theory of chain reactions makes it possible to obtain equations of such chain processes for which the changes in the concentrations of the reactants may be neglected. These equations characterize the conditions of initiation of the reaction. It is at the initial stages of a reaction that the self-ignition limits considered above appear. In the general case, taking into consideration the part played by burning out or consumption of the reactants during the reaction, we can obtain a system of non-linear differential equations in partial derivatives whose solution is quite complicated. For this reason we shall not consider such general solutions. If one reaction proceeds slowly, and the others rapidly, the system of equations is replaced by one equation that can easily be solved.

Assume that we have the cycle of transformations

$$A' \rightarrow A'' \rightarrow A''' \rightarrow A' \tag{8.62}$$

If the first reaction is a slow one, and the remaining ones proceed exceedingly rapidly, the time required for propagation of the entire cycle reduces to the time required for the propagation of the reaction $A' \rightarrow A''$. During this time in a branching process at least two molecules of A′ appear instead of one initial molecule and, in addition, one molecule of the product X. Consequently, one molecule of the product corresponds to each perishing molecule of A′ and, therefore,

$$-\frac{da'}{dt}=\frac{dx}{dt} \tag{8.63}$$

where $a'$ and $x$ are the number of molecules of A′ and X in a unit of volume at the moment $t$.

This rate determines the number of cycles propagating a second. Since the duration of propagation of a cycle is determined by the first bimolecular reaction between the active particles A′ and the initial molecules A, then

$$\frac{dx}{dt}=ka'a \tag{8.64}$$

where

$$a = a_0 - x \tag{8.65}$$

Here $a_0$ is the initial concentration of molecules of A and $x$ is the concentration of product X formed. Integration of Eq. (8.63) yields

$$a'=a_0'+x \tag{8.66}$$

where $a'$ and $x$ = concentrations of active particles and product molecules at the moment $t$, respectively

$a_0'$ = concentration of active particles at the initial moment $t = 0$.

Inserting Eqs. (8.65) and (8.66) into Eq. (8.64), we get

$$\frac{dx}{dt} = k(a_0' + x)(a_0 - x) \tag{8.67}$$

Experiments show that a great number of chain reactions obey Eq. (8.67). After integration of this equation we have

$$t = \frac{1}{k(a_0' + a_0)} \ln \frac{a_0' + x}{(a_0 - x)\, a_0''} \tag{8.68}$$

where $a_0'' = a_0'/a_0$.

If $x \gg a_0'$ and $a_0 \gg a_0'$, then neglecting the small quantities, we can write

$$t = \frac{1}{ka_0} \ln \frac{x}{a_0 a_0''} \tag{8.69}$$

or

$$x = \alpha e^{t/\tau} \tag{8.70}$$

where

$$\tau = \frac{1}{ka_0} \quad \text{and} \quad \alpha = a_0 a_0''$$

As can be seen from Eq. (8.67), the rate of such a reaction is maximum at $x = \frac{a_0 - a_0'}{2}$. This means that at the beginning the reaction proceeds with acceleration. Figure 8.6 shows a plot of the time dependence of the amount of product. The curve $x = f(t)$ has a point of inflection.

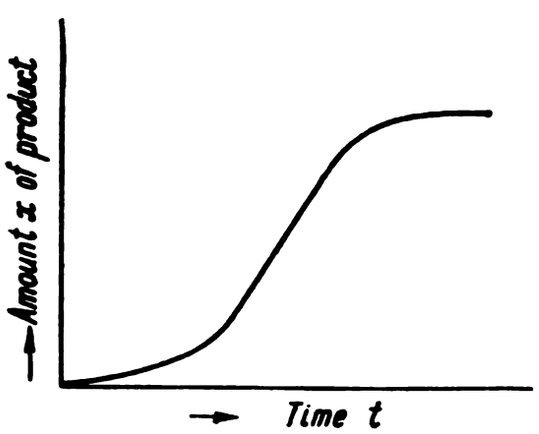


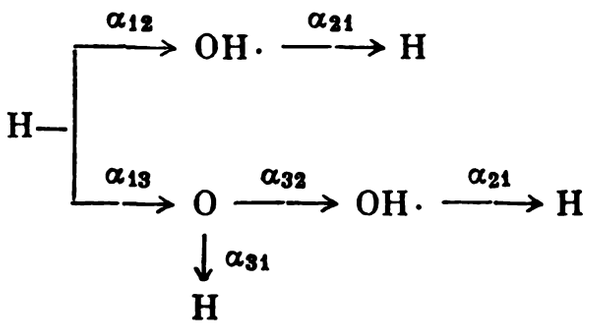

Fig. 8.6. Time dependence of amount of product for a chain chemical reaction

The concentration of atoms in branching chain reactions may become tens and hundreds of thousands of times greater than the equilibrium concentration. This was shown by V. Kondratev on the example of the rarefied flame of hydrogen at temperatures considerably lower than 1000 °C. The concentration of hydrogen atoms in such a flame reaches 10% of the total content of hydrogen in the mixture. This concentration is $10^5$ times greater than the thermodynamically stable one.

In deducing Eq. (8.67) we neglected recombination of the intermediates. If account is taken of destroying of intermediates as a result of recombination, the concentration of substance A′ may decrease toward the end of the reaction, although the amount of the product will still grow. Equation (8.67) will accordingly contain an additional negative term whose absolute value grows with an increase in the concentration of the product $x$. As shown by Semenov, such recombination can be taken into account accurately only in the simplest cases by methods of numerical integration.

Equations (8.67) and (8.68) describe the kinetics of a self-accelerating process during its entire course. Only on the basis of the equations considered in Secs. 8.5 and 8.6, however, can we say at what pressures and temperatures a branching process will be self-accelerating ($\tau > 0$) and at what ones attenuating ($\tau < 0$).

Let us consider another possible simplified derivation of the two limits of self-ignition using the probability method proposed by Akulov. For this purpose it is necessary to write the scheme of the cycle in such a way that the intermediate that led to the propagation of the cycle should be regenerated at the end of this cycle. For example, for the reaction of combustion of hydrogen, which can be depicted in the form of the sequence of reactions given in Table 8.1, the cycle can be shown schematically as follows:




This complex cycle consists of three simple ones, each of which terminates in the generation of hydrogen atoms. The probability of the fact that a given simple cycle will occur is determined by the product of the probabilities $\alpha_{ij}$ for each stage of this cycle. Thus the probability of propagation of the first cycle is

$$\delta_1 = \alpha_{12}\alpha_{21} \tag{8.71}$$

that of the second cycle

$$\delta_2 = \alpha_{13}\alpha_{32}\alpha_{21} \tag{8.72}$$

that of the third cycle

$$\delta_3 = \alpha_{13}\alpha_{31} \tag{8.73}$$

Let $\varkappa_1$ be the number of molecules of the intermediate formed during the first cycle, $\varkappa_2$ the number of molecules of the intermediate obtained if the second cycle is accomplished, etc. The propagation of all the simple cycles will thus give on an average

$$\omega = \varkappa_1\delta_1 + \varkappa_2\delta_2 + \varkappa_3\delta_3 \tag{8.74}$$

molecules of the intermediate[1] (in the example being considered all the values of $\varkappa_i$ are equal to unity).

The condition of the stationary nature of the process will be written as $\omega = 1$. This is the condition for changing of the process from an attenuating one to a self-accelerating one. For example,

[1] Here the average value is found as the *mathematical expectation of a random quantity*. By the mathematical expectation of a random quantity of the discrete type is meant *the sum of its possible values multiplied by the corresponding probabilities.*

the self-ignition of a gas mixture is possible if the process proceeds with a growth in its rate, i.e. when $\omega > 1$. Hence the condition $\omega = 1$ gives an equation for the self-ignition limits, i.e. makes it possible to establish the relation between the pressure $p$, temperature $T$ and other physical parameters characterizing such a state of a gas mixture when a corresponding, even if insignificant, change in the values of $p$ and $T$ may lead to self-ignition.

To calculate the self-ignition limits, it is necessary to find the value of $\alpha_{ij}$ with the aid of the fundamental postulate of chemical kinetics. To take into account the part played by the diameter of the vessel, the fundamental postulate of chemical kinetics should be applied not by computing the rate of a reaction in a unit of volume, as is customary practice, but by computing the rate of the given kind of reactions in the entire reacting system.

Let $u$ be the concentration of the active intermediate (for example, of hydrogen atoms, as in the scheme given above) that reacts with the reactants at the slowest rate, and $c$ the concentration of all of the reactant that reacts with the active molecules of the intermediate according to a bimolecular process. Consequently, for the rate of a reaction (the number of reacting molecules in a unit of time) in the bulk we have

$$Z_1 = k_1 ucV \tag{8.75}$$

where $V$ is the volume of the reaction vessel.

If we consider that the active intermediate is destroyed upon triple collisions, the number of such cases in the bulk will be

$$Z_2 = k_2 uc^2 V \tag{8.76}$$

In addition, the active intermediate, as indicated above, may perish as a result of collisions of the active molecules with the walls of the vessel. The number of such cases in a second will be

$$Z_3 = k_3 uA \tag{8.77}$$

where $A$ is the surface area of the walls of the vessel in which the reaction is proceeding.

The probability of each of these reactions

$$\alpha_{ij} = \frac{Z_i}{Z_1 + Z_2 + Z_3} \tag{8.78}$$

If it is assumed that the most rapidly reacting active intermediates (for example, OH and O in the above scheme) are not destroyed in the bulk and on the surface of the walls owing to their short lifetime, then $\alpha_{21} = \alpha_{32} = \alpha_{31} = 1$; since $\alpha_{12} = \alpha_{13}$, then $\delta_1 = \delta_2 = \delta_3 = \alpha_{12}$ and, therefore,

$$\omega = (\varkappa_1 + \varkappa_2 + \varkappa_3)\, \alpha_{12} \tag{8.79}$$

Inserting into this expression the value of $\alpha_{12}$, we get

$$\omega = \frac{Z_1(\varkappa_1 + \varkappa_2 + \varkappa_3)}{Z_1 + Z_2 + Z_3} \tag{8.80}$$

Knowing the value of $\omega$, we can find the rate of growth of the concentration of active centres in the initial period of a reaction, when the decrease in the reactants can still be neglected.

Indeed, assuming in accordance with Sec. 8.2 that $\omega = 1$, Eq. (8.80) can be written as follows:

$$(\varkappa_1 + \varkappa_2 + \varkappa_3 - 1)\, Z_1 - Z_2 - Z_3 = 0 \tag{8.81}$$

Insertion of the values of $Z_1$, $Z_2$ and $Z_3$ from Eqs. (8.75), (8.76) and (8.77) into Eq. (8.81) and transformations yield

$$(\varkappa_1 + \varkappa_2 + \varkappa_3 - 1)\, k_1 c - k_2 c^2 - k_3 \frac{A}{V} = 0 \tag{8.82}$$

For the case being considered $\varkappa_1 = \varkappa_2 = \varkappa_3 = 1$, therefore Eq. (8.82) can be written as follows:

$$2k_1 c - k_2 c^2 - k_3 \frac{A}{V} = 0 \tag{8.83}$$

Since the equation obtained is a quadratic one with respect to $c$, there are two values of the concentration satisfying this equation and, therefore, the initial condition that $\omega = 1$. But this condition is the one for the changing of a process from an attenuating to a self-igniting one. For this reason Eq. (8.83) is an equation of two limits of self-ignition. It gives two values of the concentrations $c_1$ and $c_2$ that limit the region of self-ignition. Ignition or, in other words, a self-accelerating process is possible in the range of concentrations $c_1 \leqslant c \leqslant c_2$. The same result can be obtained by calculating the induction period. According to the definition of the quantities $Z_1$, $Z_2$ and $Z_3$ we can write that

$$V \frac{du}{dt} = Z_1 - Z_2 - Z_3 \tag{8.84}$$

or, with account of Eqs. (8.75), (8.76) and (8.77)

$$\frac{du}{dt} = \left(k_1 c - k_2 c^2 - k_3 \frac{A}{V}\right) u = \frac{u}{\tau} \tag{8.85}$$

where

$$\tau = \frac{1}{k_1 c - k_2 c^2 - k_3 \frac{A}{V}} \tag{8.86}$$

After integration we have

$$u = u_0 e^{t/\tau} \tag{8.87}$$

The scale factor $\tau$ in exponential functions of type (8.87) is usually called the *induction period*; $u_0$ is the concentration of the active molecules at the initial moment $t = 0$.

A glance at Eq. (8.87) shows that the induction period is the time during which the concentration of the intermediate increases $e$ times.

This equation does not take into account the rate of spontaneous initiation of active centres, which in the majority of cases can be neglected. Let us consider this on the following example. Assume that we have two diatomic gases $H_2$ and $O_2$ contained in glass vessels at a sufficiently high temperature. Equilibrium of the following type will set in in each of the vessels:

$$H_2 \rightleftharpoons H + H$$
$$O_2 \rightleftharpoons O + O$$

After these gases are mixed, the atoms of oxygen and hydrogen will play the part of "seeds" initiating the chains. Besides, as a result of further dissociation of $O_2$ and $H_2$ additional atoms of H and O may form. The rate of this process is usually considerably lower than that of increase in the number of O and H atoms as a result of propagation of the chain, and this process may be neglected.

To find the temperature dependence of the induction period it is necessary to take into account the temperature dependence of the rate constant of a bimolecular reaction

$$k_1 = k_0 e^{-E/RT} \tag{8.88}$$

The activation energy of the reaction of perishing upon collision with the walls or upon triple collisions can be assumed equal to zero, i.e. it can be considered that $k_1$ and $k_3$ do not depend on the temperature. Insertion of Eq. (8.88) into Eq. (8.86) gives the equation of the induction period deduced by N. Akulov for moderate values of $c$:

$$\tau = \frac{\tau_0}{(c - c_1)(c_2 - c)} \tag{8.89}$$

where $\tau_0 = k_2^{-1}$, and $c_1$ and $c_2$ are the roots of the equation

$$k' e^{-E/RT} c - c^2 - k'' d_0^{-1} = 0 \tag{8.90}$$

in which $k' = k_0/k_2$, $k'' = k_3/k_2$ and $d_0 = V/A$ is a quantity proportional to the diameter of the vessel.

The condition of the self-ignition limits $\omega = 1$ is equivalent to the condition $\tau = \infty$. Indeed, in this case it follows from Eq. (8.87) that $u = u_0$, i.e. the process is stationary. It thus follows from Eq. (8.89) that there are two limits of self-ignition. The induction period becomes equal to infinity at the concentrations $c = c_1$ and $c = c_2$, which can be found from Eq. (8.90). From the latter equation we find that the concentrations corresponding to two ignition

limits are

$$c_{12} = \frac{1}{2} k' e^{-E/RT} \pm \sqrt{(k')^2 e^{-2E/RT} - 4k'' d_0^{-1}} \tag{8.91}$$

It follows from Eq. (8.89) that at $c < c_1$ or $c > c_2$ the parameter $\tau$ is negative, i.e. the process according to Eq. (8.87) is an attenuating one. In the region $c_1 < c < c_2$ the quantity $\tau$ is positive ($\tau > 0$), and the process will proceed with self-acceleration.

In the region of not too great values of $c$ Eq. (8.89) well agrees with experimental data. At low values of $c$ the quantity $c^2$ may be neglected in Eq. (8.90), and for this reason for the concentration corresponding to the lower limit $c_{low}$ we have

$$c_{low} = \frac{k'' e^{E/RT}}{k' d_0} \tag{8.92}$$

It should be noted that the considered deduction of the two limits relates to the case of unintensive destroying of the active particles at the walls. In intensive destroying, calculations first conducted by Semenov give an equation of the type

$$k' e^{-E/RT} c - c^2 - k'' \tau_0^{-2} c^{-1} D = 0 \tag{8.93}$$

where $D$ is the coefficient of diffusion.

At high pressures Eqs. (8.89) and (8.90) cannot be applied, since their derivation is based on the condition that triple collisions lead to the deactivation of the reactive centres.

# CHAPTER 9

# PHOTOCHEMICAL REACTIONS

**9.1. Fundamental Laws of Photochemistry.** The laws underlying the proceeding of chemical processes caused by the action of light (radiation with frequencies of the visible spectrum and with ones close to them) are considered in the branch of physical chemistry called *photochemistry*. In this branch considerable attention is devoted to the rates of photochemical reactions, and for this reason it is the most expedient to consider the fundamentals of photochemistry in the part of the book devoted to chemical kinetics.

The main process proceeding under the action of light—photodissociation, or the excitation of molecules—was dealt with in Sec. 2.2, therefore only the fundamental photochemical laws and the nature of the secondary processes will be considered below.

T. Grotthuss in Russia (1818) and J. Draper in the USA (1839) independently of each other formulated a law according to which *only those rays are chemically active that are absorbed by the reaction mixture*. This law is obvious and has no exceptions. The reverse statement that rays absorbed in a reaction are chemically active is not always true, since not all absorbed rays cause a photochemical reaction.

The Grotthuss-Draper law directly relates the chemical action of light to its absorption by a substance, and therefore it is important to know the physical aspect of the phenomenon of absorption of a light flux in semitransparent media. J. Lambert (1760) established that *the weakening of the intensity of light $dI$ that has passed through a layer with a thickness of $dl$ is directly proportional to the thickness of the layer and the intensity of the incident light $I$*, and A. Beer (1853) showed that *the absorption by a thin layer is directly proportional to the number of particles (molecules) or their concentration in the layer.*

It is easy to see that the combined Lambert-Beer law can be written in the form

$$I = I_0 e^{-knl} \tag{9.1}$$

where $I_0$ = intensity of light flux before it passes through the absorbing layer

$I$ = intensity of light flux after absorption in a layer with a thickness $l$

$k$ = proportionality factor called the *molecular absorption coefficient* or *the extinction coefficient*

$n$ = number of molecules absorbing light per cubic centimetre.

R. Bunsen and H. Roscoe (1855), investigating the reaction of formation of hydrogen chloride from hydrogen and chlorine proceeding under the action of light, established that *the chemical action of light* (expressed in the amount of product obtained) *is directly proportional to the product of the light intensity I and the duration of its action t*. This relation has an approximate nature, since not all of the light energy is always completely consumed for the chemical process. If in one case $N_1$ molecules react during the time $t_1$ at an intensity $I_1$, and in another case in the same system $N_2$ molecules react during the time $t_2$ at the intensity $I_2$, the mathematical expression of the law will be the condition

$$I_1 t_1 = I_2 t_2 \text{ when } N_1 = N_2 \tag{9.2}$$

J. van't Hoff (1904) generalized these laws. He showed that *the amount of chemically changed substance is directly proportional to the quantity of light absorbed by the system*.

The quantity of light $Q$ absorbed in a unit of time can be found from the Lambert-Beer law. Indeed, from Eq. (9.1) we have

$$Q = I_0 - I = I_0 (1 - e^{-knl}) \tag{9.3}$$

Hence, according to van't Hoff's law, the rate of a photochemical reaction ($-dn/dt$) is proportional to the quantity of light absorbed by a substance in a unit of time:

$$-\frac{dn}{dt} = K I_0 (1 - e^{-knl}) \tag{9.4}$$

where $K$ is a proportionality factor.

The most interesting and important law which has made it possible to understand the mechanism of photochemical reactions is the *Stark-Einstein law of photochemical equivalence* (1912) according to which *one transformed molecule corresponds to every absorbed quantum of radiation* $h\nu$. As will be shown below, the word transformation here implies both an energy and a chemical one.

The number of quanta absorbed in a unit of time is

$$n_a = \frac{Q}{h\nu} \tag{9.5}$$

Consequently,

$$n_r = \frac{Q}{h\nu} \tag{9.6}$$

molecules should transform under the action of light.

**9.2. Quantum Yield.** Experiments show that frequently the number of molecules reacted is not equal to the number of quanta absorbed. For this reason the concept of *quantum efficiency* or *quantum yield* $\gamma$ was introduced to characterize photochemical reactions. *The quantum yield is the ratio of the number of molecules that have reacted to the number of absorbed quanta*, i.e.

$$\gamma = \frac{n_r}{n_a} = \frac{n_r}{Q/h\nu} \tag{9.7}$$

The rate of a chemical reaction, according to Eq. (9.7), is

$$-\frac{dn}{dt} = \frac{dn_r}{dt} = \gamma \frac{dn_a}{dt} = \gamma \frac{Q}{h\nu} \tag{9.8}$$

Inserting Eq. (9.3) into Eq. (9.8), we get

$$-\frac{dn}{dt} = \gamma \frac{I_0}{h\nu}(1 - e^{-knl}) \tag{9.9}$$

This is the most general expression for the rate of a photochemical reaction that combines all the laws of photochemistry and gives a theoretical interpretation of the proportionality factor in Eq. (9.4).

**9.3. Main Types of Photochemical Processes.** Tables 9.1 and 9.2 present a selection of typical photochemical reactions in the gaseous phase and in solutions. Experiments show that all photochemical reactions can be divided into four groups according to the value of the quantum yield, namely, (1) reactions in which the quantum yield $\gamma = 1$ (for example, the formation of bromo-cyclohexane, hydrogen peroxide, nitrosomethane, bromine as a result of the reaction of chlorine with trichlorobromomethane, the decomposition of hydrogen sulphide in a benzene solution, etc.); (2) reactions in which the quantum yield $\gamma < 1$ (for example, the decomposition of ammonia, methyl iodide and bromide, acetone, acetic acid, the formation of hexabromobenzene); (3) reactions in which the quantum yield $\gamma > 1$ (for example, the formation of sulphuryl chloride, hydrogen bromide, ozone, the decomposition of hydrogen bromide, nitrogen dioxide, azomethane, hypochlorous acid, etc.); and (4) reactions in which the quantum yield $\gamma \gg 1$ (for example, the reactions of chlorine with hydrogen and with carbon monoxide, etc.).

Deviation of the quantum yield from unity, however, does not denote deviation from the law of photochemical equivalence. As shown by experiments, a photochemical process consists of a primary process caused by absorption of a light quantum and, as a rule, leading to the dissociation of a molecule and to the formation of free atoms and radicals, and of secondary processes caused by free atoms and radicals formed during the primary process entering into a reaction. The secondary processes may consist in deactivation of the

TABLE 9.1

**Parameters of Selected Photochemical Reactions in the Gaseous Phase**

| Reaction | Substance absorbing light | Wavelength, Å | Quantum yield $\gamma$ |
|---|---|---|---|
| $Cl_2 + H_2 \rightarrow 2HCl$ | $Cl_2$ | 3030-5000 | $10^4$-$10^6$ |
| $Cl_2 + O_2 \rightarrow O_2Cl_2$ | $Cl_2$ | 4200 | 1 |
| $Cl_2 + CO \rightarrow COCl_2$ | $Cl_2$ | 4000-4360 | $10^3$ |
| $Cl_2 + SO_2 \rightarrow SO_2Cl_2$ | $Cl_2$ | 4200 | 2-3 |
| $Br_2 + H_2 \rightarrow 2HBr$ | $Br_2$ | 5000-5780 | 0-2 |
| $Br_2 + C_6H_{12} \rightarrow C_6H_{11}Br + HBr$ | $Br_2$ | 4700 | 1 |
| $2HBr \rightarrow H_2 + Br_2$ | HBr | 2070-2537 | 2 |
| $\frac{3}{2} O_2 \rightarrow O_3$ | $O_2$ | 2070-2537 | 2 |
| $O_2 + H_2 \rightarrow H_2O_2$ | $O_2$ | 1719-1725 | 1 |
| $2NH_3 \rightarrow N_2 + 3H_2$ | $NH_3$ | 2000-2200 | 0.14-0.2 (at 20 °C); 0.5 (at 500 °C) |
| $2NO_2 \rightarrow 2NO + O_2$ | $O_2$ | 3130-4050 | 2 |
| $CH_3I \rightarrow (CH_4, C_2H_6, I_2)$ | $CH_3I$ | 2026-2100 | 0.01 |
| $CH_3Br \rightarrow (CH_4, Br_2)$ | $CH_3Br$ | 2537 | $4 \times 10^{-3}$ |
| $2CH_3Br + 2NO \rightarrow 2CH_3NO + Br_2$ | $CH_3Br$ | 2537 | 1 |
| $CH_3COCH_3 \rightarrow (C_2H_6, CO, CH_4)$ | $CH_3COCH_3$ | 3130 | 0.2 |
| $CH_3-N=N-CH_3 \rightarrow C_2H_6 + N_2$ | $CH_3-N=NCH_3$ | 3130 | 2 |

TABLE 9.2

**Parameters of Selected Photochemical Reactions in Solutions**

| Reaction | Solvent | Substance absorbing light | Wave-length, Å | Quantum yield $\gamma$ |
|---|---|---|---|---|
| $Cl_2 + 2CCl_3Br \rightarrow 2CCl_4 + Br_2$ | $CCl_4$ | $Cl_2$ | 4700 | 1 |
| $2ClO_2 \rightarrow Cl_2 + 2O_2$ | $CCl_4$ | $ClO_2$ | 4100 | 2 |
| $2HClO \rightarrow 2HCl + O_2$ | $H_2O$ | HClO | 3660-4360 | 2 |
| $C_6H_6 + 3Br_2 \rightarrow C_6H_6Br_6$ | $C_6H_6$ | $Br_2$ | 3000-5500 | 0.4-0.9 |
| $2H_2O_2 \rightarrow 2H_2O + O_2$ | $H_2O$ | $H_2O_2$ | 2750-3660 | 20-500 |
| $H_2S \rightarrow H_2 + S$ | $H_2O$ | $H_2S$ | 2070-2530 | 0.2-0.3 |
| | $C_6H_{14}$ | $H_2S$ | 2070-2530 | 1 |
| $CH_3COOH \rightarrow CH_4 + CO_2$ | $H_2O$ | $CH_3COOH$ | 1850-2300 | 0.5 |

molecules excited upon the absorption of light quanta, or in the recombination of atoms and radicals. The primary photochemical processes, which are truly photochemical ones, always obey the Stark-Einstein equivalence law. Thus, deviation of the quantum

yield from unity denotes not deviation from the law of equivalence, but the appearance of secondary processes which, changing the value of the quantum yield, proceed without the absorption of light.

The quantum yield of reactions proceeding in solutions or in gases at very low pressures is very frequently less than unity. For reactions in solutions this is due to deactivation of the molecules excited in the transfer of energy to molecules of the solvent or to recombination of the atoms and molecules formed in photochemical dissociation, the recombination being facilitated by molecules of the solvent that play the part of third particles. Such destroying of reactive particles has been called the Franck-Rabinowitch *cell effect*.

If a reaction proceeds in gases under a low pressure with the participation of excited molecules, the active molecules formed may become deactivated by emitting light before they collide with the reacting molecules. In the photochemical decomposition of ammonia, the quantum yield depends on the temperature. When the temperature changes from 20 to 500 °C, the value of $\gamma$ changes from 0.2 to 0.5. This can be explained by the following circumstances. The primary process of the absorption of a photon is accompanied by the detaching of one of the hydrogen atoms:

$$NH_3 \xrightarrow{+h\nu} NH_2\cdot + H$$

after which secondary processes may occur, namely,

$$NH_2\cdot + H \longrightarrow NH\cdot + H_2 \qquad \text{(a)}$$

$$NH\cdot + NH\cdot \longrightarrow N_2 + H_2 \qquad \text{(b)}$$

leading to the formation of hydrogen and nitrogen. The following process of recombination, however, is also possible:

$$NH_2\cdot + H \longrightarrow NH_3 \qquad \text{(c)}$$

Its probability at room temperature is three times greater than that of process (b). Thus, three-fourths of the active products of photolysis are returned to the initial state (ammonia molecules). This process leads to a reduction in the quantum yield, which becomes less than unity. With a growth in temperature the probability of recombination drops somewhat, which leads to the increase of the quantum yield.

In a number of cases the quantum yield is greater than unity. It is frequently equal to two or three. Examples of such photochemical processes are the reactions of decomposition of hydrogen iodide and bromide in the gaseous phase:

$$2HI \xrightarrow{+h\nu} H_2 + I_2$$

$$2HBr \xrightarrow{+h\nu} H_2 + Br_2$$

or the reaction of decomposition of nitrosyl chloride

$$2NOCl \xrightarrow{+h\nu} 2NO + Cl_2$$

for which $\gamma = 2$.

The photochemical decomposition of hydrogen bromide and iodide belongs to photochemical reactions whose mechanism is known the best. The primary process consists in the dissociation of the hydrogen halide into atoms:

$$HI \xrightarrow{+h\nu} H + I$$

The following reactions are possible for the atoms of H and I produced:

| | | |
|---|---|---|
| $H + HI \rightarrow H_2 + I$ | $\Delta H^\circ = -32.1$ kcal/mol | (a) |
| $H + I_2 \rightarrow HI + I$ | $\Delta H^\circ = -33.7$ " | (b) |
| $I + H_2 \rightarrow HI + H$ | $\Delta H^\circ = +32.1$ " | (c) |
| $I + HI \rightarrow I_2 + H$ | $\Delta H^\circ = +33.7$ " | (d) |
| $H + H \rightarrow H_2$ | $\Delta H^\circ = -101.9$ " | (e) |
| $I + I \rightarrow I_2$ | $\Delta H^\circ = -35.6$ " | (f) |
| $I + H \rightarrow HI$ | $\Delta H^\circ = -69.8$ " | (g) |

Only reaction (a) is significant for the hydrogen atoms, since if $I_2$ is removed from the sphere of the reaction, reaction (b) has practically no importance. Owing to the low concentration of both reactants, the same is true for reactions (e) and (g). Only reaction (f) is possible for the iodine atoms, since owing to the endothermic nature of reactions (c) and (d) the activation energy is very great. Reaction (g) is impossible owing to the low concentration of the hydrogen atoms, which are mainly consumed according to reaction (a). For this reason the proceeding reaction consists in a complex of the following processes:

$$\begin{array}{rcl} HI & \xrightarrow{+h\nu} & H + I \\ H + HI & \longrightarrow & H_2 + I \\ I + I & \longrightarrow & I_2 \\ \hline 2HI & \xrightarrow{+h\nu} & H_2 + I_2 \end{array}$$

The quantum yield of the reaction is thus equal to two. The iodine atoms produced in the elementary photochemical process recombine according to reaction (f), and molecular iodine is formed.

If molecular iodine is added beforehand to the hydrogen iodide, the process of decomposition of the hydrogen iodide will retard owing to reaction (b).

A quantum yield close to two ($\gamma = 1.76$) has also been obtained for an $0.8N$ solution of HI in hexane. The decomposition of hydrogen iodide proceeds with a reduced quantum yield in different solvents (water, hexane) and in condensed hydrogen iodide, although the mechanism remains the same. This is shown in Table 9.3.

TABLE 9.3

**Parameters of Photochemical Decomposition of Hydrogen Iodide in the Gaseous Phase and in Solutions**

| Medium | Wavelength, Å | Quantum yield $\gamma$ |
|---|---|---|
| Gaseous phase | 2070-2820 | 2 |
| HI, liquid | 3000 | 1.84 |
| Solution in $C_6H_{14}$, $0.8N$ | 2220 | 1.52 |
| Ditto | 2820 | 1.78 |
| Solution in $H_2O$, $0.8N$ | 2220 | 0.078 |
| Ditto | 2820 | 0.114 |

We have already considered the cause of this phenomenon. It is interesting that the quantum yield grows with an increase in the wavelength. This is explained by a reduction in the probability of exciting the solvent molecules with a reduction in the radiation energy initiating the decomposition of the hydrogen iodide.

For some reactions the quantum yield was found to be equal to three. An example of such a reaction is the formation of ozone from oxygen (under a pressure of 47.5 atm), which apparently proceeds as follows:

$$O_2 \xrightarrow{+h\nu} O_2^*$$

$$O_2^* + 2O_2 \rightarrow 2O_3$$

Sometimes the quantum yield may be of the order of several tens. For example, the photochemical polymerization of gaseous acetylene proceeds with a quantum yield of $\gamma = 9.2$; for the reactions of decomposition of hydrogen peroxide in water the quantum yields range from 7 to 500. The detailed mechanism of reactions for which $\gamma > 1$ is frequently unknown.

An example of reactions for which $\gamma \gg 1$ is the reaction of combination of chlorine with hydrogen that we have already considered in Sec. 8.1. For this reaction $\gamma \approx 10^5$, i.e. about one hundred thousand transformed molecules of chlorine and hydrogen correspond to one absorbed quantum.

The differences between photochemical and ordinary (in the dark) reactions can be illustrated on the example of the formation of hydrogen bromide. The reaction $H_2 + Br_2 \rightarrow 2HBr$ proceeding in

the dark has been investigated in detail within the temperature interval of 200-300 °C and was found to consist of the following elementary steps:

$$Br_2 \xrightarrow{k_1} Br + Br \qquad \Delta H^\circ = +45.2 \text{ kcal/mol} \tag{a}$$

$$Br + H_2 \xrightarrow{k_2} HBr + H \qquad \Delta H^\circ = +16.2 \quad " \tag{b}$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br \qquad \Delta H^\circ = +40.5 \quad " \tag{c}$$

$$H + HBr \xrightarrow{k_4} H_2 + Br \qquad \Delta H^\circ = -16.2 \quad " \tag{d}$$

$$Br + Br \xrightarrow{k_5} Br_2 \qquad \Delta H^\circ = -45.2 \quad " \tag{e}$$

Applying Bodenstein's stationary-state principle, the mechanism of this reaction can be described by the kinetic equation

$$\frac{d[HBr]}{dt} = \frac{2\frac{k_2k_3}{k_4}[H_2]\sqrt{\frac{2k_1}{k_5}[Br_2]}}{\frac{k_3}{k_4} + \frac{[HBr]}{[Br_2]}} \tag{9.10}$$

that well satisfies experimental data. It can be seen that the rate of the reaction at the beginning of the process, when $[Br_2] \gg [HBr]$, is directly proportional to $\sqrt{2k_1[Br_2]}$, i.e. to the square root of the rate of process (a), as a result of which the bromine atoms initiating the entire process are formed.

The photochemical reaction proceeds quite well already at room temperatures when a mixture of hydrogen and bromine is illuminated with light having a wavelength exceeding 5000 Å. The rate of the photochemical reaction exceeds that of the reaction in the dark about 500 times.

The elementary process of the photochemical reaction differs in the way the bromine atoms are formed, namely, thermal process (a) is replaced by the photolysis of the molecular bromine:

$$Br_2 \xrightarrow{+h\nu} Br + Br \tag{a'}$$

It is quite obvious that when there is an excess of bromine molecules, each quantum of radiation causes the formation of two bromine atoms. The rate of formation of the active particles thus depends only on the density of radiation, i.e. on the concentration $[h\nu]$. When process (a) is replaced by process (a′), the rate of the reaction is expressed by the kinetic equation

$$\frac{d[HBr]}{dt} = \frac{2\frac{k_2k_3}{k_4\sqrt{k_5}}[H_2]\sqrt{2[h\nu]}}{\frac{k_3}{k_4} + \frac{[HBr]}{[Br_2]}} \tag{9.11}$$

which completely describes the photochemical reaction in the same way as Eq. (9.10) describes the reaction in the dark. These equations indicate that the secondary processes in both cases are completely of the same type, and differ only in the way the bromine atoms are formed.

It is obvious that in all photochemical reactions the primary photochemical process obeys the Stark-Einstein equivalence law; the nature of the deviation from this law makes it possible to understand the secondary processes which are not photochemical ones.

Closely related to primary photochemical processes are the so-called sensitized reactions, in which the molecules directly absorbing radiant energy do not participate. They delegate this function to their neighbouring molecules which by themselves are not sensitive to radiation of the given frequency and receive energy from the molecules that directly absorb it. An example of such a process is the previously considered dissociation of molecular hydrogen in the presence of mercury vapour whose atoms absorb light corresponding to the resonance line of mercury with a wavelength of $\lambda = 2536.7$ Å. At present a great number of sensitized reactions are known. In addition to mercury vapour, the sensitizers include the halogens, chlorophyll and iron ions.

In photochemical reactions equilibrium shifts under the action of light, which changes the rates of the forward and reverse reactions. As a result of the absorption of light, the store of free energy in the system changes, and also its equilibrium constant. It is obvious that an appreciable violation of equilibrium can be observed only when the quantum yield of a reaction is close to unity.

# CHAPTER 10

# REACTIONS IN ELECTRICAL DISCHARGES

**10.1. Appearance of a Discharge in a Gas. Kinds of Self-Maintained Discharge.** If a potential difference is created between electrodes placed in a gas and is gradually increased, the weak current appearing in the circuit will initially obey Ohm's law (Fig. 10.1). The appearance of this current is the result of the so-called initial electrical conductivity of the gas due to the presence of charged particles—ions—in it. The ions are constantly formed under the action of external ionizers (light, cosmic and radioactive radiation, etc.). With a further increase in the potential gradient $E$, the current stops depending on the voltage and becomes almost constant, equal in value to the saturation current. The current is constant at a value of $E$ at which all the charged particles formed in the space between the electrodes, and also the particles getting into this space from outside, have time to reach the electrodes before they are destroyed.

This phenomenon is called *semi-self-maintained discharge*, since the current disappears upon elimination of the action of the external ionizers.

At a certain higher value of the potential gradient, however, the current again begins to grow. This value of $E$ is directly proportional to the pressure of the gas and depends on its nature. At a potential gradient corresponding to the value $A$ (see Fig. 10.1) a *silent* or *Townsend discharge* begins, which is characterized by very low currents and almost complete absence of glowing of the gas. A weak glow is nevertheless observed, since the electrons, acquiring the ability of ionizing the molecules, can also, naturally, excite them.

Upon a further increase in the potential gradient (see Fig. 10.1) the current first grows relatively slowly, but at a definite value of the potential gradient equal to $B$ it sharply leaps to very high values mainly determined by the external resistance of the circuit and the power of the current source. Simultaneously a bright glow of the gas is observed. This phenomenon, which occurs, for example, in air at atmospheric pressure and a value of the potential gradient of the order of $3 \times 10^4$ V/cm, is called the *ignition of a gas discharge* or *breakdown of the gas gap*.

The discharge forming after the breakdown is a *self-maintained* one, since it itself produces charged particles by avalanche ioniza-

tion, and no external ionizers are required for maintaining the current.

During a breakdown, the electrical conductivity of the gas gap becomes very great, and the voltage across the electrodes sharply drops to the so-called *discharge burning voltage*. Depending on a number of conditions, a self-maintained discharge may be characterized by its appearance, the nature of the elementary processes and the distribution of the field intensity along the axis of the discharge. The basic forms of a self-maintained discharge are a spark, glow and arc discharge.

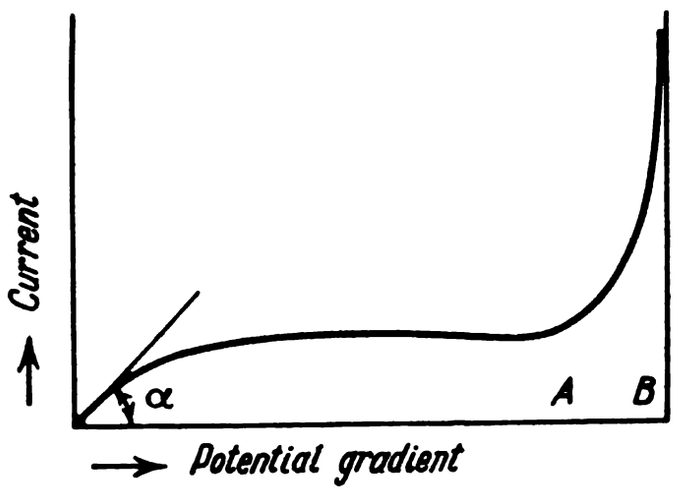



Fig. 10.1. Dependence of current intensity on potential gradient in semi-self-maintained discharge and upon transition to self-maintained discharge

At high pressures of the gas (of the order of atmospheric and higher), great distances between the electrodes, a high-voltage but low-power source of current (for example, an induction coil) a *spark discharge* occurs accompanied by a characteristic crackling sound.

At low pressures of the gas (several millimetres of mercury) and a not very low resistance of the external circuit, a *glow discharge* is formed. If the resistance of the external circuit is not great, the power of the source of current is sufficient and the pressure of the gas is higher, then after breakdown an *arc discharge* is formed. A glow discharge can be gradually changed into an arc discharge by increasing the current (by reducing the external resistance of the circuit) and simultaneously increasing the pressure. Here different forms of a glow discharge can be obtained.

These are the kinds of discharge observed after *complete* breakdown of the gas gap. In special conditions a self-maintained discharge may form at voltages much lower than the breakdown one. This is observed in non-uniform fields with electrodes of a small radius of curvature—thin wires or points (for example, a thin wire coaxially arranged inside a hollow cylinder). With such a configuration and mutual arrangement of the electrodes, the potential gradient will be the greatest at the surface of the wire, decreasing toward the cylinder inversely proportional to the distance from the axis of the wire. Thus, near the wire it may be sufficient for breakdown to occur, and far from it, i.e. closer to the surface of the cylinder, it may be too low. In this case a *self-maintained corona discharge* accompanied by a characteristic hissing noise appears in a thin layer around

the wire. Outside of the glowing layer electron avalanches do not develop, and here the current is conducted only by charges of the same sign as the charge of the corona electrode that penetrate from the glowing region. In other words, the discharge remains semi-self-maintained outside of the region of glowing. With an increase of the voltage, the current of the corona discharge grows, the glowing layer extends and finally complete breakdown occurs. Thus the current in the corona is limited not by the resistance of the external circuit, as in the forms of self-maintained discharge listed above, but by the low electrical conductivity of the external non-glowing layer. In a number of features, i.e. in the nature of the glow, the low current density, the shape of the volt-ampere characteristic, the low mean temperature of the gas and the sound effects, a corona discharge is similar to another special form of self-maintained discharge that will be described in a later section—the *barrier discharge*.

Historically the spark discharge was the first form of discharge in a gas to be used for conducting chemical reactions. A very great number of reactions were studied with its aid, including diverse reactions of synthesis (the synthesis of $NH_3$, NO, HCN, $O_3$, etc.) and reactions of transformation and decomposition of hydrocarbons. These investigations, however, mainly followed preparation purposes and were only of a qualitative nature. It has been shown, for example, that at the very high temperature developing in the spark channel the gas molecules decompose into atoms and radicals. Getting into a medium with a lower temperature and interacting with the initial molecules, and also with one another, these active particles may initiate different reactions. Quantitative investigation of the chemical action of a spark discharge is quite difficult for a number of reasons, and to date has practically not been conducted.

**10.2. Chemical Reactions in a Glow Discharge. Obtaining of Atomic Hydrogen and Other Free Radicals.** Chemical reactions proceeding at a constant pressure and a sufficiently high temperature are known to be accompanied by a decrease in the Gibbs energy ($G$) and proceed to a state of equilibrium characterized by the minimum value of $G$. To achieve a degree of dissociation of molecular hydrogen into atoms equal to 0.5 at a pressure of 0.001 atm, the hydrogen must be heated to about 2600 K. At a temperature of 800 K an equilibrium mixture contains altogether about $10^{-8}$ per cent of atoms.

Practically complete dissociation of hydrogen can be obtained in a glow discharge at gas temperatures considerably below 800 K, i.e. concentrations of the atoms that are greater than the equilibrium values for the given temperature. This also relates to many other chemical reactions—the dissociation of oxygen and chlorine into atoms, the decomposition of various compounds ($H_2O$, $NH_3$, hydrocarbons) into free radicals, the synthesis of nitrogen oxide

from the elements, etc. This possibility of obtaining concentrations of the products above the equilibrium ones is due to the non-isothermal nature of the discharge plasma, to the existence of a very high temperature of the electron gas in addition to the relatively low temperature of the molecular gas. It is this difference of temperature in the gas that makes it possible to obtain a non-equilibrium state.

The specific mechanism of using the energy of the electron gas for activating a chemical process is obviously different in different reactions. In particular, the mechanism of dissociation of hydrogen molecules is probably as shown in Fig. 10.2. Upon collision with an electron, a hydrogen molecule passes[1] from the normal singlet state $^1\Sigma_g^+$ to the triplet state $^3\Sigma_g^+$. For this, the electron should have a minimum energy of 11.4 eV, which corresponds to a temperature of 85 000 K. Since the reverse spontaneous transition is forbidden by the selection rules, a molecule performs an allowed transition from the upper level to the unstable state $^3\Sigma_u^+$, dissociates into normal atoms and radiates the excess energy in the form of a continuous spectrum in the ultraviolet region.

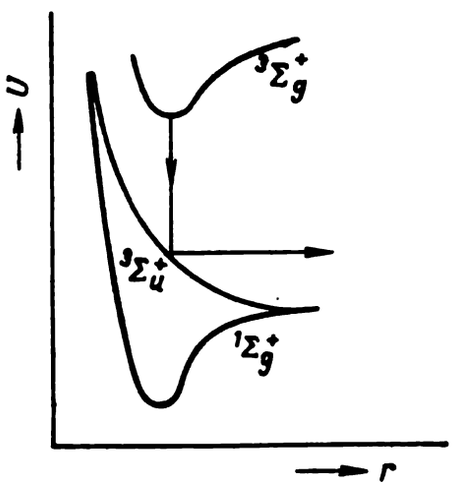



Fig. 10.2. Dissociation of hydrogen into normal atoms upon collision with an electron

It is also possible to obtain various simple free radicals in a glow discharge, such as hydroxyl from water, methyl and methylene from methane, etc. The combined action of a glow discharge and a low temperature (about —195 °C) makes it possible to obtain ozone from oxygen, and a solid glassy substance containing, as it has been established, the higher hydrogen peroxide $H_2O_4$, from water.

**10.3. Chemical Reactions in an Arc Discharge.** With an increase in the pressure and current, the molecular temperature grows, and the electron temperature decreases, i.e. the difference between these temperatures gradually disappears. In such conditions an arc discharge is formed.

The most important practical application of a high-temperature arc is the so-called electrocracking of methane to acetylene, proceeding according to the equation

$$2CH_4 = C_2H_2 + 3H_2$$

[1] In collisions with electrons the quantum forbiddenness is not observed so strictly as in the absorption and emission of light.

This is an essentially endothermal reaction ($\Delta H^{\circ}_{298}$ = 90 kcal/mol $C_2H_2$), which is conducted in a d-c arc in a reactor shown schematically in Fig. 10.3. About 2800 cubic metres of methane an hour are blown into the upper chamber of the reactor through tangentially arranged inlets *3* at a high velocity under a pressure of 1.5 atm. The motion of this stream is accompanied by rotation, and continues in the channel of lower electrode *2* cooled outside by water. The powerful d-c arc (7000 V, 1000 A) ignited by means of auxiliary electrode *4* extends to a length of about one metre between the upper insulated electrode (cathode) *1* and the lower part of the earthed electrode *2*. The reaction proceeds mainly in the channel of the latter, where the gas comes into contact with the arc. During one passage through the reactor about half of the initial methane is transformed. The products, containing on an average about 13.0% $C_2H_2$, 1% $C_2H_4$, 50% $H_2$ and 30% (by volume) of unreacted methane, and also a certain amount of soot, leave the arc after being heated to 1600 °C. Since the acetylene itself is not stable at such temperatures, the gases in chamber *5* are cooled to 150 °C by the direct injection of water.

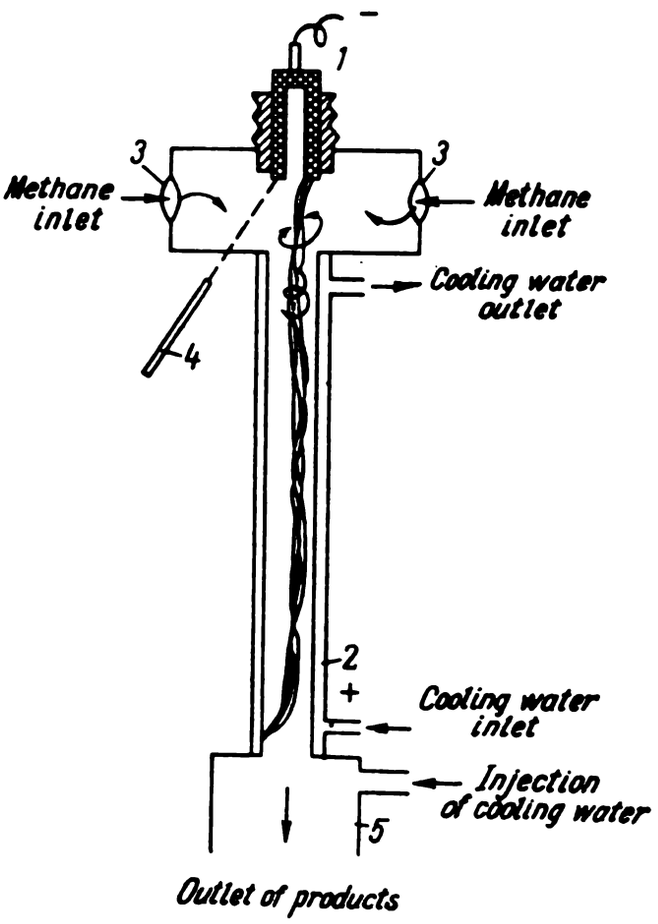



Fig. 10.3. Reactor for electrical cracking of methane to acetylene:
*1*—cathode; *2*—earthed electrode; *3*—gas inlets; *4*—auxiliary electrode; *5*—chamber

The consumption of energy in the arc (which together with the concentration of the acetylene is the main technical and economical index of the process) is about 10 kWh per kilogramme of acetylene, i.e. it is approximately equal to the consumption of energy when producing acetylene in the usual way (from calcium carbide).

An installation similar to that shown in Fig. 10.3 can also be used for the synthesis of nitrogen oxide in a high-temperature arc. Here, in contrast to the reaction in a glow discharge, the concentrations of the nitrogen oxide do not exceed the equilibrium ones. The industrial synthesis of nitrogen oxide by this method, widely used at the beginning of the present century, is no longer used at present owing to the excessively great expenditure of energy.

**10.4. Chemical Reactions in a Pulsed Discharge at Low Pressures. Active Nitrogen.** If a second auxiliary gap is connected in series with the main discharge gap, and a large-capacity capacitor is connected in parallel to it, it is possible to obtain bursts of current and briefly developing power up to $2 \times 10^7$ kW. Such a discharge is called a *condensed* or *pulsed* one.

Nitrogen subjected to the action of a pulsed discharge acquires a higher chemical activity and continues to glow during a rather long time even after the discharge is stopped. The presence of considerable concentrations of atomic nitrogen (up to 40%) has been found by direct measurements in such afterglowing nitrogen. The nature of active nitrogen is more complicated, however, and to date cannot yet be considered as finally established.

Active nitrogen forms nitrides with many elements, and ammonia with hydrogen. The formation of ammonia proceeds especially intensively on metal surfaces if the hydrogen is also in the atomic state. Halogens do not react with active nitrogen, the same as HCl, but HBr and HI decompose in its presence, the reaction being accompanied by glowing. Water, carbon dioxide and carbon monoxide do not react with active nitrogen, while ammonia in its presence rapidly decomposes. Nitrogen oxide partly decomposes and partly transforms into $N_2O_3$, this reaction being accompanied by green luminescence.

Organic substances (ether, acetylene, benzene, pentane, heptane, halogen derivatives of hydrocarbons—chloroform, methyl bromide, ethyl chloride, etc.) react with active nitrogen to form hydrocyanic acid. In particular, the reaction of active nitrogen with acetylene apparently proceeds as follows:

$$C_2H_2 + 2N = 2HCN$$

Active nitrogen can also be obtained in considerably lower concentrations in continuous discharges, for example in an ordinary glow or high-frequency electrodeless discharge.

**10.5. Chemical Reactions in a Barrier Discharge.** When a high-voltage alternating current is fed to electrodes separated by dielectric plates and a gas gap, a so-called *barrier discharge* appears in the latter. A prototype of an apparatus using such a discharge is an ozonizer. This kind of discharge has polymerizing action. Liquid and solid products are formed in it from low-molecular hydrocarbons, and hydrogen peroxide from hydrogen and oxygen. The synthesis of ozone from oxygen is the best studied and practically the most important reaction conducted in a barrier discharge. This is a reversible endothermic reaction:

$$\frac{3}{2} O_2 \rightleftharpoons O_3; \ \Delta H = 34.5 \text{ kcal/mol } O_3$$

which apparently proceeds from left to right in two steps. The first step is an endothermic one and consists in the dissociation of the oxygen molecules into atoms:

$$O_2 \rightarrow 2O;\ \Delta H = 118.2 \text{ kcal/mol } O_2 \quad (1)$$

$$O + O_2 + M \rightarrow O_3 + M;\ \Delta H = -24.6 \text{ kcal/mol } O_3 \quad (2)$$

The best results are obtained when the reaction is conducted in all-glass ozonizers if the gap between the barriers is equal to about 1 mm. At a coolant temperature close to room temperature, the stationary concentration of the ozone reaches 10.5% (by volume). When the temperature is reduced to —40 °C the stationary concentration grows to 16%. The energy yield of ozone at low concentrations reaches 200 g or approximately 4 mol of $O_3$ per kWh.

**10.6. Kinetics of Reactions in Electrical Discharges.** The kinetics of endothermic reactions in electrical discharges has been studied best of all. For example:

$$2CH_4 = C_2H_2 + 3H_2$$

$$N_2 + O_2 = 2NO$$

$$3O_2 = 2O_3$$

These reactions will be the main ones discussed in the present section.

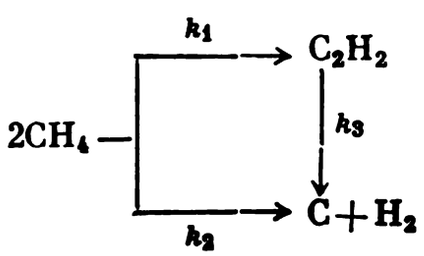
In the first stage of studying the kinetics of gas reactions in electrical discharges (the 1920's), scientists attempted to draw an analogy between these reactions and electrolysis in solutions. The proportionality between the amount of reactant and the current observed in some instances made it possible to formulate a law of electrochemical equivalence similar to Faraday's laws. It was soon found, however, that Faraday's laws cannot be applied to reactions in electrical discharges.

Investigations led to the formulation of the fundamental postulate supplementing (for reactions in electrical discharges) the known laws of chemical kinetics, namely, *the rate of a chemical reaction in a given kind of electrical discharge is proportional to the power of the discharge.*

The limitation expressed by the words "in a given kind of electrical discharge" should be understood to mean that a change in the power must not lead to a change in the kind of discharge. The proportionality factors for the same reaction in different kinds of discharge may have absolutely different values. For example, at a low pressure a glow discharge is very slightly effective with respect to the reaction of transformation of methane into acetylene, while an arc discharge at medium pressures is quite effective. For this reason, if a change in power caused, for example, by a change in pressure and current, leads to transition of a glow discharge into an arc one, the proportionality factor sharply grows. The main diffi-

culty in studying the kinetics of reactions in a discharge consists in that it is practically impossible to accurately determine the duration of the reaction. The matter is that the actual volume of the reaction zone is unknown. This difficulty was overcome by including the value of the volume $V$ of the reaction zone in the rate constant, i.e. by substituting for the duration of a reaction in the kinetic equations a quantity proportional to it, namely, the inverse volume rate of flow of a gas through the reaction vessel ($1/V$).

*Kinetics of Electrical Cracking of Methane.* Experiments show that in the electrical cracking of methane the main reaction of formation of acetylene is supplemented by reactions such as the formation of other unsaturated compounds, among which ethylene predominates, and the decomposition of the hydrocarbons into elements. The kinetics of the transformation of methane and the accumulation of acetylene, however, can in the first approximation be shown by the following kinetic diagram, regardless of the mechanism of the reactions:




The diagram shows that methane participates in two parallel reactions, while acetylene is the intermediate of two consecutive reactions. The concentration of the acetylene, or the degree of transformation of methane into acetylene, should pass through a maximum according to the diagram, which is entirely confirmed experimentally.

The summary rate of transformation of methane will be written as follows:

$$-\frac{dN_{CH_4}}{dt}=(k_1+k_2)\,uN_{CH_4} \qquad (10.1)$$

and the rate of accumulation of acetylene

$$\frac{dN_{C_2H_2}}{dt}=\frac{1}{2}k_1uN_{CH_4}-k_3uN_{C_2H_2} \qquad (10.2)$$

where $N$ = number of moles of the respective gases
$k_1$, $k_2$ and $k_3$ = rate constants of the corresponding first-order reactions
$u$ = power of discharge.

Equations (10.1) and (10.2) take into account the proportionality between the rate of a reaction and the power of the discharge.

Integration of Eq. (10.1) from 0 to $t$ and from $N_0$ to $N_{CH_4}$ yields

$$N_{CH_4} = N_0 e^{-(k_1+k_2)ut} \tag{10.3}$$

In accordance with what has been said above, let us replace the duration of the reaction $t$ with a quantity that is the reciprocal of the volume rate of flow of the gas ($1/V$) (which will of course result in a change in the numerical value and dimension of the constants $k_1$ and $k_2$). After simple transformations we shall obtain an expression for the total degree of transformation of methane $\Delta$:

$$\Delta \equiv \frac{N_0 - N_{CH_4}}{N_0} = 1 - e^{-(k_1+k_2)\frac{u}{V}} \tag{10.4}$$

Thus, the quantity $\Delta$ is now expressed as a function of the specific energy, i.e. of the ratio $u/V$, which is the amount of energy per unit of volume of the initial gas in standard conditions.

After inserting $N_{CH_4}$ from Eq. (10.4) into Eq. (10.2), integration and similar transformations, we get an expression for the degree of transformation of methane into acetylene:

$$\gamma \equiv \frac{2N_{C_2H_2}}{N_0} = \frac{k_1}{k_1+k_2-k_3}\left[1 - e^{-(k_1+k_2-k_3)\frac{u}{V}}\right] e^{-k_3\frac{u}{V}} \tag{10.5}$$

Finally, let us express the consumption of energy per cubic metre of acetylene ($\alpha$) reduced to standard conditions as a function of the specific energy. It can be shown that

$$\alpha \equiv \frac{u}{V}\frac{2}{\gamma} = \frac{2(k_1+k_2-k_3)\frac{u}{V} e^{+k_3\frac{u}{V}}}{k_1\left[1 - e^{-(k_1+k_2-k_3)\frac{u}{V}}\right]} \frac{\text{kWh}}{\text{m}^3\text{C}_2\text{H}_2} \tag{10.6}$$

if the power is expressed in kilowatts, and the rate of flow of the gas in cubic metres an hour.

Let us consider the dimension and physical meaning of the constants $k_i$ in Eqs. (10.4), (10.5) and (10.6). Since the constants are multipliers together with the specific energy in the dimensionless exponents, their dimension is the reciprocal of that of $u/V$, i.e. it essentially differs from the dimension of the rate constants in the usual equations of chemical kinetics. Thus, if $u/V$ is expressed in kilowatt-hours per cubic metre of gas reduced to standard conditions, the dimension of $k_i$ will be cubic metres per kilowatt-hour.

The constants being discussed characterize the ability of a discharge to perform a chemical transformation per unit of energy spent. In this connection it was proposed to call them the *energy effectiveness of the chemical action of a discharge.*

Figure 10.4 compares the results of calculations according to Eqs. (10.4), (10.5) and (10.6) (solid curves) with experimental data

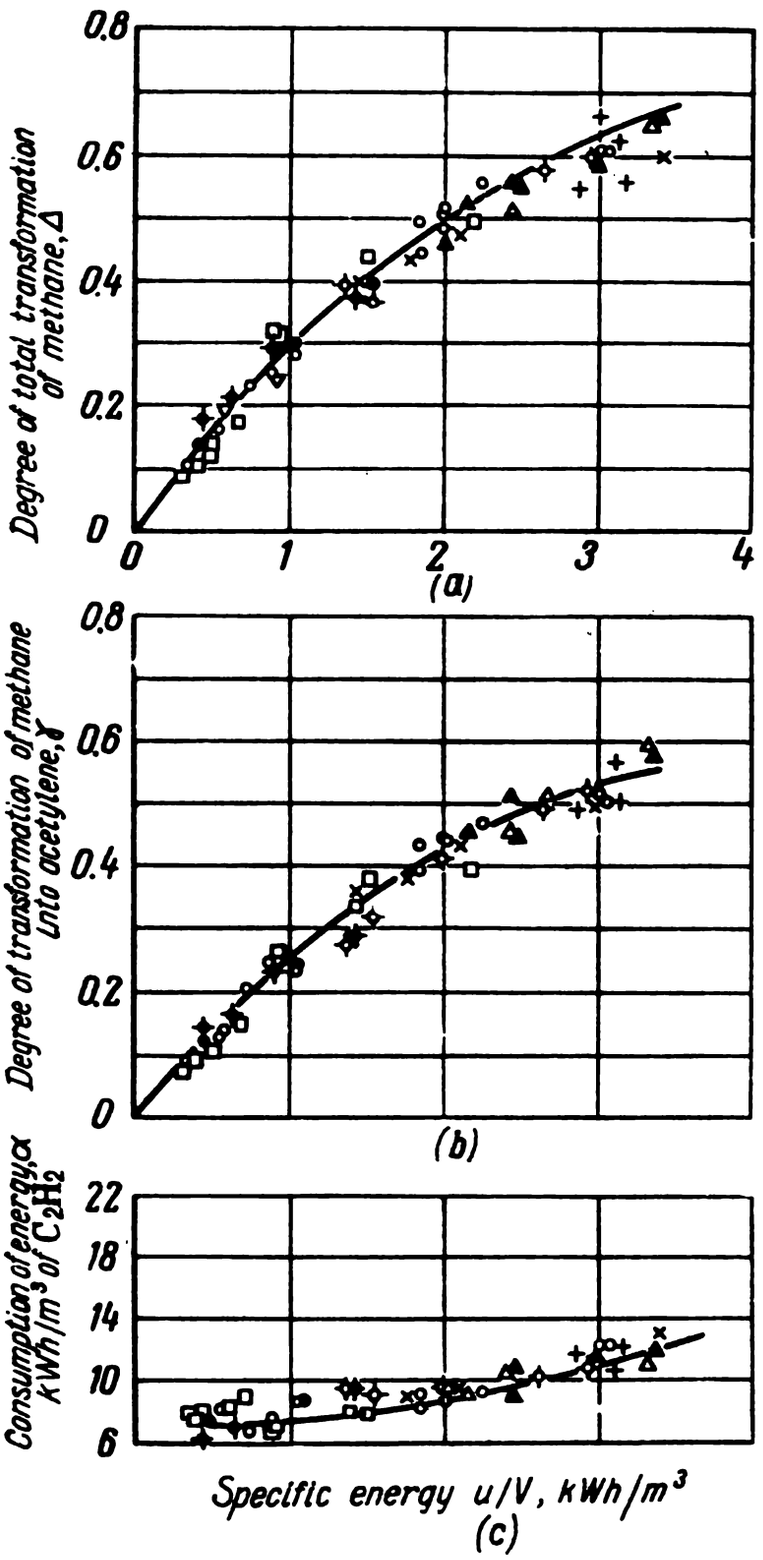



Fig. 10.4. Degree of total transformation of methane (Δ), degree of transformation of methane into acetylene (γ) and consumption of energy for producing 1 m³ of acetylene (α) versus specific energy

(different symbols corresponding to different experiments) for the electrical cracking of methane to acetylene. The experiments were conducted in a three-phase arc at a reduced pressure changing in the different series of experiments from 40 to 150 mm Hg. The arc current was changed from 0.5 to 5 A, and the distance between electrodes from 18 to 55 cm. Notwithstanding such a variety of the conditions, the experimental data are satisfactorily described by the calculated curves, i.e. are functions of only $u/V$. The experimentally found values of the constants are $k_1 = 0.317$, $k_2 = 0.026$ and $k_3 = 0.058$ m³/kWh.

The total energy effectiveness of a discharge with respect to the transformation of methane, i.e. the sum $k_1 + k_2$, is here equal to 0.343 m³/kWh.

A close value of $k_1 + k_2$, namely 0.373 m³/kWh, was obtained in other experiments and in absolutely different apparatus, but also in an arc discharge and at a reduced pressure. At a pressure close to atmospheric, the sum $k_1 + k_2$ was found to be equal to 0.196 m³/kWh. Thus, with an increase in the pressure, the energy effectiveness of an arc with respect to the electrical cracking of methane decreases. The transition of the arc to a glow discharge with a low current at a low pressure also leads to a reduction in the energy effectiveness.

*Kinetics of Nitrogen Oxide Synthesis.* In compiling the kinetic equation for the reversible reaction $N_2 + O_2 \rightleftarrows 2NO$, let us denote the concentration of the nitrogen oxide by $x$ and include the slightly changing concentration of the nitrogen and oxygen in the constant $K_1$; let us also assume a second-order reaction of decomposition of NO. Hence

$$\frac{dx}{at} = K'_1 u - K'_2 u x^2 \tag{10.7}$$

Integration of this equation at a constant discharge power $u$ and substitution of the inverse velocity of the gas flow $1/V$ for $t$ yield

$$x = \left(\frac{K_1}{K_2}\right)^{1/2} \frac{1 - e^{-2(K_1K_2)^{1/2}\frac{u}{V}}}{1 + e^{-2(K_1K_2)^{1/2}\frac{u}{V}}} \tag{10.8}$$

This equation agrees with the limiting conditions characterizing the experimental dependence of the per cent of nitrogen oxide on the specific energy, and in a number of cases describes experimental data quite well. In other cases a first-order reaction of decomposition of nitrogen oxide corresponds better to the results of experiments. Here instead of Eq. (10.8) we get the equation

$$x = \frac{K_1}{K_2}\left(1 - e^{-K_2\frac{u}{V}}\right) \tag{10.9}$$

*Kinetics of Synthesis of Ozone in a Barrier Discharge. Influence of an Admixture of a Foreign Gas.* For the reversible reaction of formation of ozone ($^3/_2O_2 \rightleftarrows O_3$), the dependence of the degree of transformation $\Delta$ of oxygen into ozone is expressed by an equation similar to Eq. (10.9) (with the same assumptions):

$$\Delta = \frac{K_1}{K_2}\left(1 - e^{-K_2\frac{u}{V}}\right) \tag{10.10}$$

Of great importance is the investigation of the kinetics of synthesis of ozone from mixtures of oxygen with argon and oxygen with nitrogen. Here in Eq. (10.10) the energy should be related to the partial volume of the oxygen $u/V_{O_2}$. This allows us to establish the independence of the kinetic constants and the degree of transformation of oxygen into ozone on the composition of the gas mixture. The argon thus plays the part of an inert diluent that does not consume energy.

Entirely different results are obtained in studying the synthesis of ozone from mixtures of oxygen and nitrogen. It was found that upon a change in the content of nitrogen in its mixture with oxygen, the stationary degree of transformation of the latter into ozone passes

through a sharply expressed maximum corresponding to 68% of $N_2$. Consequently, nitrogen acts here as an activator. This is especially obvious at comparatively low contents of nitrogen in the mixture, when in comparison with pure oxygen not only great degrees of transformation, but also great absolute concentrations of ozone are obtained. For example, the other conditions of the experiments being equal, the stationary content of ozone in technical oxygen (about 0.5% $N_2$) is 5.3%, and in a mixture containing 19% of $N_2$ it was 6.5%. The presence of nitrogen apparently facilitates the more effective utilization of the energy spent in the discharge for the synthesis of ozone. There obviously exists a certain mechanism of transfer of the energy absorbed by the nitrogen to the oxygen molecules being activated. This mechanism will be discussed in the following section in connection with the so-called *theory of energy catalysis.*

**10.7. Mechanism of Chemical Reactions in Discharges.** The diversity of conditions in different electrical discharges, from a low-temperature glow discharge at a low pressure to an exceedingly powerful pulsed discharge in which the temperature reaches $10^6$ °C apparently does not allow us to speak of a universal theory of chemical reactions in electrical discharges. No such theory exists, but the main directions of the theoretical investigation can be outlined.

The source of energy in a discharge is an electric field, which first of all imparts acceleration to the free electrons. The latter, in turn, transfer their energy to the molecules of the gas upon elastic and inelastic collisions. The inelastic collisions result in excitation, ionization, and dissociation of the molecules into free radicals or atoms. In principle any of these particles, i.e. an excited molecule, an ion or a free radical, may be a chemically active particle participating in a primary elementary act. Depending on the conditions, the primary act may be followed by various *secondary* reactions, the latter developing not only in the plasma[1] of the discharge itself, but also on the walls of the discharge tube. Thus the quite complicated task of studying the mechanism of reactions in a discharge consists, firstly, in establishing the nature of the primarily active chemical particle and that of the primary elementary act, and, secondly, in studying the possible secondary reactions. It should be kept in mind that the plasma of a discharge may or may not be isothermal. In isothermal plasma the temperature of the electron and molecular gases is the same, and the action of the electric field consists only in imparting to the plasma, naturally through the electron gas, an energy sufficient to maintain the high temperature. In such

[1] A plasma is a gas which is composed of a nearly equal number of positive and negative free charges (positive ions and electrons). A plasma is formed, for example, in the positive columns of a glow or an arc discharge.

a "hot" isothermal plasma the concentrations of the different particles are determined by thermodynamic equilibrium. They can be calculated according to the usual thermodynamic equations if the corresponding equilibrium constants and temperatures are known. The mechanism of chemical reactions in an isothermal plasma does not differ from that of reactions proceeding at a high temperature created in the system in any other way. Here we speak of the thermal activation of the reactions in a discharge. Sometimes, for example in a condensed spark and in the microdischarges of a barrier discharge, the active particles formed during the short current pulses may then get into a medium with a considerably lower temperature, initiate secondary reactions in it leading to the formation of products whose concentrations will essentially differ from the equilibrium ones at the primary temperature of formation of the active particles. Nevertheless here also the nature of primary activation is a thermal one.

In a relatively cold non-isothermal plasma, for example in a glow discharge, in which the temperature of the electron gas exceeds the temperature of the molecular gas to some extent, the concentrations of the particles, some of which may be chemically active, are determined not by thermodynamic equilibrium, but by a stationary state which is due to competition between the various processes of the formation and destroying of particles. Depending on the ratio between the rates of the oppositely directed processes, the concentrations of both the primarily active particles and of the products inside the plasma itself may considerably exceed the thermally equilibrium values. Here it will be appropriate to speak of the specific electrical activation of reactions, which is what will be considered in the present section.

The first idea of the nature of chemically active particles in a discharge considered them to be identical with ions. Purely ionic mechanisms were also postulated for a number of reactions in a glow discharge, namely,

$$N_2+2O_2 \rightleftarrows 2NO_2, 3O_2, \rightleftarrows 2O_3, \quad 2CO+O_2 \rightleftarrows 2O_2,$$
$$2CH_4 \rightleftarrows C_2H_4+2H_2, \text{ etc}$$

In its initial form, however, the ionic hypothesis sometimes contradicts the law of conservation of energy. For example, in the electrical cracking of methane to acetylene in a glow discharge, an energy of the order of 7 kWh per cubic metre of $C_2H_2$ produced is required. Let us assume that the ionization of one molecule of $CH_4$ or the expenditure of energy equal to 14.5 eV is necessary and sufficient for the formation of one molecule of $C_2H_2$. Now even if we make the absolutely inconceivable assumption that the energy of the discharge is completely used for the formation of acetylene, we get a consumption of energy equal to 17.3 kWh per cubic metre of $C_2H_2$.

In general there are no special grounds to consider ions to be more reactive than molecules (except, perhaps, for cases when the ions can be considered as free radicals, for example $N_2^+$), since for most of the positive diatomic ions studied, the bond energies are greater and the internuclear distances are smaller than the same quantities in molecules.

S. Lind proposed an altered ionic theory of the mechanism of the chemical action of a discharge called the *theory of ionic groups* or *of complex ions*. According to this theory[1], molecules having either a constant dipole moment or a moment induced by the field of an ion group around it, i.e. the system is a complex ion preserved as a single whole in electrostatic fields. Upon collision with a particle having a charge of the opposite sign, the ion becomes neutralized, and the liberated energy is used for chemical activation of the molecules surrounding it. For example, according to Lind, water vapour may decompose as follows

$$H_2O^+ + 4H_2O \longrightarrow (H_2O)_5^+$$

$$(H_2O)_5^+ + e \longrightarrow 5H_2 + \frac{5}{2}O_2$$

Thus, there are five decomposed molecules of water for every primary ion $H_2O^+$. The law of conservation of energy is not violated, since the ionization potential of an $H_2O$ molecule is 13 eV, and an energy approximately equal to $5 \times 2.5 = 12.5$ eV is required for the decomposition of five molecules of $H_2O$. According to the "hot point" theory worked out by V. Livingston (1936), the complex is heated to a high temperature due to the energy liberated upon the neutralization of the central ion, i.e. immediately after neutralization the complex has the energy that it would have if it existed in the form of a great mass of gas at a certain equivalent temperature. Naturally, the small number of molecules forming the complex is not sufficient for determining the temperature in its usual statistical sense. All the complexes in the reacting system when considered together, however, allow statistical consideration.

Thus, ascribing a definite high temperature to a totality of neutralizing complexes, Livingston considers that chemical equilibrium sets in in the complexes. This theory was used to explain reactions under the action of alpha-particles, in particular the reactions of formation and decomposition of hydrogen bromide. It can be shown, however, especially for non-polar molecules, that the possibility itself of the formation of a complex ion as a stable whole is doubtful.

N. Kobozev, S. Vasilev and E. Eremin (in the theory of energy catalysis, 1937) assumed that for reactions in discharges there is no

[1] A similar theory was worked out independently by the Soviet physicochemist N. Nekrasov.

necessity of searching for any special chemically active particles differing from the active ones in ordinary thermal reactions, i.e. that the active particles in a discharge can be the same as in ordinary reactions (free atoms, free radicals and vibrationally excited molecules). But the ways of formation of these particles in a discharge and, consequently, their concentrations may be absolutely different than in ordinary reactions.

It is interesting to note that the reactions of synthesis and decomposition of hydrogen bromide under the action of alpha-particles explained by the theory of hot points were described with still greater success by H. Eyring and his collaborators (1936) by an atomic mechanism given below in an abbreviated form:

$$\left.\begin{array}{l} H_2 + \alpha \rightarrow 2H + \alpha \\ Br_2 + \alpha \rightarrow 2Br + \alpha \\ HBr + \alpha \rightarrow H + Br + \alpha \\ H_2 + \alpha \rightarrow 2H^+ + e + \alpha \\ Br_2 + \alpha \rightarrow 2Br^+ + e + \alpha \end{array}\right\} \text{Primary processes}$$

$$\left.\begin{array}{l} H + Br_2 \rightarrow HBr + Br \\ H + HBr \rightarrow H_2 + Br \\ e + Br_2 \rightarrow Br^- + Br \\ e + HBr \rightarrow Br^- + H \end{array}\right\} \text{Secondary processes}$$

M. Bodenstein (1938) explained the fact that the yield of nitrogen oxide exceeds the equilibrium one when it is synthesized in an arc discharge at a pressure of the order of 100 mm Hg by the formation of nitrogen and oxygen atoms as a result of collisions between the molecules and electrons. E. Eremin paid attention to the circumstance that in the electrical cracking of methane to acetylene the *thermochemical efficiency of the discharge* $\eta$, i.e. the ratio of the heat of the reaction to the energy actually spent in the discharge, has relatively high values. For the reaction $2CH_4 = C_2H_2 + 3H_2$ the value of $\eta$ reaches 0.7, for other endothermal reactions in a discharge the efficiency is considerably lower, and for the reactions of synthesis of nitrogen oxide and ozone the value of $\eta$ does not exceed 0.04 and 0.11, respectively. Such a high value of the efficiency in electrical cracking can be explained if we assume that chain reactions propagate with the participation of atoms and radicals. In particular, the following mechanism was considered:

$$\begin{array}{c} CH_4 \rightarrow CH_3 + H \\ H + CH_4 \rightarrow CH_3 + H_2 \\ CH_3 \rightarrow CH_2 + H \\ CH_3 + CH_2 \rightarrow CH{=}CH_2 + H_2 \\ CH = CH_2 \rightarrow CH{\equiv}CH + H \text{ etc.} \end{array}$$

The formation of atoms and radicals in discharges was in many cases directly confirmed by the mass spectrometric method.

The considerations set out above, however, do not completely explain the mechanism of the chemical action of a discharge. Chemi-

cally, the free atoms and radicals are different particles in comparison with the initial molecules. Reactions with their participation are secondary ones. In many respects the mechanism of the primary reactions of the formation of atoms and radicals remains unclear. It is quite probable that different mechanisms of splitting of the molecules are possible. Sometimes, as for example in the dissociation of hydrogen, the process directly begins upon collision with an electron. Dissociation is also possible due to the saturation of affinity of one of the atoms to an electron, i.e. a process of the type

$$e + X_2 \rightarrow X^- + X$$

or

$$e + HX \rightarrow X^- + H$$

where X is a halogen atom.

The part of a free radical is sometimes played by an ion, for example the ion $N_2^+$, which is a biradical. Here a primary process of ionization by an electron impact leads to the formation of a radical. According to the theory of *energy catalysis* mentioned above, a significant part in reactions proceeding in discharges is played by the so-called collisions of the second kind, as a result of which the energy of electron excitation of one of the participants transforms into a different kind of energy of the other one. An example of a collision of the second kind in a discharge is the process occurring in a discharge in a mixture of argon and oxygen

$$Ar^* (3P) + O_2 (^3\Sigma) \rightarrow Ar (^1S) + O^* (^1D) + O (^1S)$$

when an oxygen molecule dissociates into atoms upon collision with an excited argon atom. It is also known that the mercury vapour sensitizes the dissociation of hydrogen molecules in collisions with electrons. Thus, without mercury an appreciable dissociation of $H_2$ begins only at an activation energy of at least 11.4 eV, and with mercury at 7.7 eV. This can be explained by the following sequence of processes:

$$e\ (7.7\ \text{eV}) + Hg\ (6\ ^1S_0) \rightarrow Hg\ (7\ ^3S_1) + e\ (0\ \text{eV})$$

$$Hg\ (7\ ^3S_1) \rightarrow Hg \left(\frac{6\ ^3P_0^0}{4.64\ \text{eV}}\right) + h\nu\ (4047\ \text{Å or } 3.06\ \text{eV})$$

$$Hg \left(\frac{6\ ^3P_0^0}{4.64\ \text{eV}}\right) + H_2 \left(^1\Sigma_g^+\right) \rightarrow 2H + Hg(^1S_0)$$

The metastable mercury atom in the state $6\ ^3P_0^0$ with an excitation energy of 4.64 eV formed in the second step gives up this energy in the third step for the dissociation of an $H_2$ molecule.

Another experimental substantiation of the theory of energy catalysis is the sensitizing action of various additions in reactions in electrical discharges. Thus, in the electrical cracking of methane in a glow discharge a considerably increased

yield of acetylene was observed in the presence of mercury vapour. The mechanism of such a "catalytic" action of the mercury vapour probably also consists in the primary formation of a metastable mercury atom and the following sensitized dissociation of a molecule of methane:

$$Hg(6\ ^3P_0^0) + CH_4 \longrightarrow CH_3 + H + Hg(^1S_0)$$

The action of mercury and sodium vapours on the decomposition of ammonia in a glow discharge, and also of mercury, zinc and cadmium vapours on its synthesis from nitrogen and hydrogen was also studied. It was found that in both cases only the mercury vapour has a sensitizing action, the decisive role belonging to the metastable atom $Hg^*$. Since the energy of breaking the N—H bond in ammonia is equal to 3.6 eV, the energy of excitation of $Hg^*$ is quite sufficient for tearing away the hydrogen in a collision of the second kind. The first step of the process of sensitized decomposition of ammonia can be shown by the following equation:

$$Hg^* + NH_3 \rightarrow NH_2 + H + Hg$$

It is assumed that the synthesis of ammonia is achieved in the reaction of excited nitrogen ($N_2^*$) with hydrogen atoms, and that the part played by the mercury consists in sensitizing the formation of the latter. As a whole the process in the presence of mercury can be shown as follows:

$$\left.\begin{array}{l} Hg + e \longrightarrow Hg^* + e \\ N_2 + e \longrightarrow N_2^* + e \end{array}\right\} \text{Excitation by collision with an electron}$$

$$Hg^* + H_2 \longrightarrow H + H + Hg \quad \text{Transfer of energy from the sensitizer to the reacting molecule}$$

$$N_2^* + H \longrightarrow NH + N$$

and further

$$NH + H_2 \longrightarrow NH_3$$

and

$$N + H_2 \longrightarrow NH + H$$

Still another example of sensitization of a reaction in a discharge, namely the increase in the yield of ozone in the presence of nitrogen, was considered in Sec. 10.6. The part of the energy catalyst is probably played by an electron-excited molecule of nitrogen in the metastable state ($N_2^*$), and the process of formation of ozone can be written as follows:

$$O_2 + e \longrightarrow O + O^* + e \quad (1)$$

$$O_2 + O + M \longrightarrow O_3 + M \quad (2)$$

$$O_3 + M \longrightarrow O_2 + O + M \quad (3)$$

$$N_2 + e \longrightarrow N_2^* + e \quad (4)$$

$$N_2^* + N_2 \longrightarrow 2N_2 \quad (5)$$

$$N_2^* + O_2 \longrightarrow N_2 + O + O \quad (6)$$

According to this scheme, ozone is formed as a result of reaction (2) upon a triple collision between a molecule and an atom of oxygen and a third particle M taking the excess energy. The part of the nitrogen consists in sensitizing the process of formation of atomic oxygen in a collision of the second kind, which is shown by reaction (6).

Thus, according to the theory of energy catalysis, a considerable part in the formation of chemically active particles in a discharge (free atoms in the examples considered above) may be played by electron-excited atoms and molecules, mainly, as is most probable, in the metastable state. The analogy with catalysis consists in that the particles with the electron-excited states themselves do not participate directly in the act of chemical reaction, but serve only as transmitters of energy from the electron gas of the discharge plasma to the molecules being activated, thus facilitating the formation of activated complexes. In the examples given above the part of the energy catalysts is played by the atoms and molecules of the added substances. Similar functions can also be fulfilled by electron-excited participants of the reaction by transferring energy in collisions of the second kind to like molecules or to molecules of other participants of the reaction. For example, the following process is possible in the synthesis of ammonia:

$$N_2^* + H_2 \longrightarrow N_2 + H + H$$

in which the part of the energy catalyst is played by a nitrogen molecule. Most probably the extreme state of activation of the molecules, i.e. their dissociation into atoms, is not always essential. Sometimes, for example in collisions of the second kind, etc., molecules may appear that are at high levels of vibrational excitation. Such molecules may also be chemically active.

CHAPTER 11

# CHEMICAL ACTION OF HIGH-ENERGY RADIATION (RADIATION CHEMISTRY)

**11.1. General.** The branch of physical chemistry devoted to a study of chemical reactions under the action of high-energy radiation is called *radiation chemistry*. The particles causing chemical reactions include neutrons, electrons, positively and negatively charged ions and quanta of energy greater than 50 eV (x-rays and $\gamma$-rays)[1]. Chemical reactions proceeding under the action of high-energy radiation are called *radiolysis*.

Although the action of radiation was first detected in 1896 (A. Becquerel noted the blackening of a photographic plate under the action of the radiation of potassium uranyl sulphate), research into the action of radiation on chemical reactions was conducted on a limited scale owing to the absence of sufficiently intensive sources of such radiation. Only in recent years, with the development of nuclear power engineering, were investigations of the action of high-energy radiation on substances undertaken on a broad scale. The first industrial processes using this radiation have been created.

**11.2. Sources of Radiation.** The waste produced in the operation of a nuclear reactor can serve as a source of high-energy radiation used in radiation chemistry. The fission of every nucleus of $^{235}U$ produces two new nuclei with approximately equal masses. These products form a group of isotopes with mass numbers from 72 to 162. The atoms of the fission products are unstable; in the process of $\beta$-decay one chemical element transforms into another one. Sometimes the nucleus formed after the emission of a $\beta$-particle is in an excited state. The transition of such a nucleus to the normal or basic state is accompanied by the emission of one or several $\gamma$-quanta. The maximum energy of $\beta$-particles emitted by the fission products is equal to 3.5 MeV, and the energy of the $\gamma$-rays to 3.8 MeV. It is short-lived fission products, however, that mainly have such an energy.

Radiolysis may also be conducted inside the active zone of an atomic reactor. About 10% of the energy liberated in a reactor is $\beta$- and $\gamma$-radiation. The sources of radiation in reactors are (a) the products of decay of the nuclear fuel (fissionable material); (b) the flows of fuel in the external circuits of reactors using liquid fuel (a solution of uranyl salts—uranyl nitrate or uranyl sulphate in water); (c) the active zone of the reactor. The discharged solid fuel can also be used in radiolysis.

Other sources of radiation are some artificially prepared radioactive isotopes, in particular $^{60}Co$. Such radioactive substances are produced in nuclear reactors

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[1] Radiation chemistry does not deal with the action of light, the energy of whose quanta does not exceed 12 eV.

when different materials are irradiated with neutrons. Depending on the duration of irradiation with neutrons, a preparation with a definite content of the isotope $^{60}Co$, i.e. a preparation with a definite activity, can be produced. The half-life of $^{60}Co$ is 5.3 years. The energies of the $\gamma$-rays of $^{60}Co$ are equal to 1.16 and 1.30 MeV.

In addition, protons, deutrons and $\alpha$-particles accelerated in special accelerators (cyclotron, van de Graaf generator) can be used as high-energy radiation. Beams of fast electrons can be produced in electron accelerators or by using the radioactive isotopes of certain elements (for example, $^{90}Sr$ and $^{137}Cs$). Powerful x-ray tubes can also serve as a source of high-energy quanta, in addition to the artificially prepared radioactive elements indicated above. The deceleration of fast electrons produced in accelerators (betatron, electron accelerator, van de Graaf generator) can also be used for obtaining $\gamma$-radiation. In addition to nuclear reactors, radium-beryllium and polonium-beryllium sources or special neutron accelerators may serve to produce neutrons.

**11.3. Difference between Radiolysis and Photolysis.** The energy of the particles employed in radiation chemistry exceeds many times the energy of the quantum levels of the valence electrons in the substances participating in a chemical reaction. For this reason, in contrast to photochemical processes (photolysis), the primary action of the high-energy radiation on the substance is not of a selective nature. This primary act usually leads to ionization of the substance and to the appearance of free radicals. The absorption of ionizing radiation depends on the atomic number of the absorbing element. The primary products are formed along the paths of the ionizing particles, the ionization growing toward the end of the path of the particles and depending on their nature and mass. In photochemical reactions the secondary processes are purely chemical ones (reactions of radicals) in the majority of cases. In contrast to photolysis, the substances appearing under the action of high-energy radiation are subjected to the further action of the radiation. The secondary processes in radiolysis may be processes of interaction of the electrons, recoil nuclei or quanta of a lower energy produced during the primary act with the substance.

**11.4. Primary Processes.** The passing of all kinds of radiation through a substance results in the particles and quanta losing energy. As long as the energy of the particles and quanta is greater than the energy of ionization of the molecules and atoms, it is mainly used for ionization of the latter.

The deceleration of $\alpha$-particles in substances is mainly due to the interaction of these particles with electrons. The latter are captured by the $\alpha$-particles with the formation of singly charged ions and electrically neutral atoms of helium. But owing to the tremendous velocity of the particles, the captured electrons are split off; this process repeating many times. Simultaneously ions are formed from the atoms and molecules of the absorbing medium. An $\alpha$-particle uses up an energy equal on the average to 34 eV for the formation of

a pair of ions in air. The electrons knocked out by $\alpha$-particles from atoms and molecules have a great kinetic energy and can themselves cause ionization of atoms and molecules.

Beta-particles have a greater penetrating power than $\alpha$-particles and a much smaller one than $\gamma$-rays. When they pass through a substance, $\beta$-particles also knock electrons out of atoms and molecules, and the latter are transformed into positively charged ions. Along their path in air $\beta$-particles form hundreds of times less pairs of ions than $\alpha$-particles along the same path. Beta-radiation can be used for practical purposes if it is necessary to ionize only the surface layer of the irradiated substance or initiate a chain chemical reaction in a gas. Where it is essential that the radiation penetrate to a great depth, for example for conducting chemical reactions in liquids and solids, $\gamma$-rays should be used.

Gamma-rays are absorbed in a substance according to one of three mechanisms. If the energy of the $\gamma$-quanta is about 10 keV ($\lambda > 1.5$ Å) a photoelectric effect is observed upon the interaction of a photon with an atom. The kinetic energy of the knocked out electron is equal to the energy of the absorbed photon less the energy required for knocking the electron out of the atom. The photon is completely absorbed and, consequently, such a process does not change the energy of the photons in the passing beam, but only reduces the total number of photons. With an increase in the energy of the incident photons, the Compton effect begins to play an appreciable part. A photon collides with an atomic electron and undergoes elastic scattering, the energy of the incident quantum being distributed between the recoil electron and the scattered photon. The released electron causes further ionization of the substance. In the Compton effect the total number of photons remains unchanged, although their energy decreases (the wavelength $\lambda$ increases), and, in addition, the direction of their motion changes. These scattered photons can also cause ionization of the substance. The probability of Compton recoil depends on the number of electrons per unit of cross-sectional area of the substance.

When the $\gamma$-quanta have an energy exceeding 1.02 MeV ($\lambda < 10^{-2}$ Å), a third process—the formation of pairs—is more probable. A photon transforms into an electron-positron pair. As in the photoelectric effect, the photon completely disappears upon the formation of a pair.

Since x-rays differ from $\gamma$-quanta only in a lower frequency and a correspondingly lower energy, the same can be said about their primary action on a substance as about low-energy $\gamma$-rays.

Neutrons passing through a substance collide and interact only with the atomic nuclei and can be absorbed by the latter. The element will thus be converted into an isotope. Decay of the nuclei of these isotopes may result in the formation of new elements. If

a neutron is not captured by a nucleus, it may eject an atom from a molecule. The velocity of the ejected atom may be so great that it may lose one or several electrons. At low energies of the neutrons the velocity of the ejected atom is not great, and it retains its electron shell, although the latter may become excited.

**11.5. Absorbed Dose. Exposure. Power of Dose.** The changes occurring in an irradiated substance under the action of various kinds of radiation depend on the amount of energy absorbed by the substance. The amount of energy of any kind of radiation absorbed by one gramme of a substance is called the *absorbed radiation dose* or simply the *absorbed dose*. Its units are the J/kg (SI system) and erg/g (cgs system). The *rad*, a unit equal to 100 ergs of energy absorbed by one gramme of any substance (regardless of the kind of ionizing radiation), is also used. Derived units of the rad are the *millirad* (1 mrad = $= 10^{-3}$ rad = 0.1 erg/g = $10^{-5}$ J/kg) and the *microrad* (1 μrad = $= 10^{-6}$ rad = $10^{-4}$ erg/g = $10^{-8}$ J/kg).

It is convenient to use the mean absorbed dose for calculations:

$$D = \frac{NEt \times 1.6 \times 10^{-6}}{100 d\rho} \text{ rad} \qquad (11.1)$$

where $N$ = number of particles impinging on 1 cm$^2$ of surface of the irradiated volume a second
$E$ = mean energy of impinging particles, MeV
$t$ = duration of irradiation, s
$1.6 \times 10^{-6}$ = thermal equivalent of 1 MeV (1 MeV = $1.6 \times 10^{-6}$ erg)
100 = energy equivalent of 1 rad (1 rad = 100 erg/g)
$d$ = length of path of ionizing particle in the irradiated substance, cm
$\rho$ = density of irradiated substance, g/cm$^3$.

The dose absorbed in a unit of time is called the *power of the absorbed dose* and is usually measured in rad/h, rad/min and rad/s. The corresponding unit in the SI system is W/kg, and in the cgs system erg/s·g.

To describe x-rays and γ-rays from the viewpoint of the ionization they produce, a quantity called *radiation exposure* or simply *exposure* is used. Its unit in the cgs system is the *roentgen* (r)—the exposure to x-rays or γ-rays at which the related corpuscular emission per 0.001 293 g of air (1 cm$^3$ of atmospheric air at 0 °C and 760 mm Hg) produces ions carrying a charge of one electrostatic unit in the air. The corresponding unit in the SI system is coulomb per kilogramme (C/kg).

Derived units of the roentgen are the *milliroentgen* (1 mr = $10^{-3}$ r) and the *microroentgen* (1μr = $10^{-6}$ r).

The charge of a single-charged ion is $4.8 \times 10^{10}$ cgse$_Q$ (the charge of an electron), therefore one roentgen forms in one cubic centimetre

of air

$$n_i = \frac{1}{4.8 \times 10^{10}} \approx 2.08 \times 10^9 \text{ pairs of ions}$$

The energy spent for the formation of one pair of ions is equal on an average to 34 eV, consequently an exposure of one roentgen corresponds to the absorption of energy equal to

$$E = 2.08 \times 10^9 \times 34 = 7.07 \times 10^{10} \text{ eV} = 0.113 \text{ erg}$$

or in one gramme of air

$$E = \frac{0.113}{0.001\,293} = 87 \text{ erg/g}$$

Consequently, the energy absorbed in air at an exposure of 1 r is equal to 87 erg/g, or the absorbed dose is equal to 0.87 rad.

Radiation exposures with an energy up to 3 MeV may be measured in roentgens.

**11.6. Activity of Radioactive Isotope.** The activity of a radioactive isotope is characterized by a unit called the *curie* (c). This unit is defined as the amount of a radioactive substance in which $3.7 \times 10^{10}$ disintegrations a second occur. Derived units are the *millicurie* (1 mc $= 10^{-3}$ c $= 3.7 \times 10^7$ d/s) and the *microcurie* (1 μc $= 10^{-6}$ c $= 3.7 \times 10^4$ d/s).

Still another unit is used to characterize the activity of γ-radiation—*a gramme-equivalent of radium*. This unit is defined as the amount of a radioactive substance which in identical geometrical conditions creates the same dose as one gramme of radium in equilibrium with its products of decay.

**11.7. Secondary Processes.** The detailed mechanism of radiolysis is not known at present. However, the basic processes that proceed under the action of any radiation are known. They include the ionization and excitation of molecules and their following dissociation with the formation of free radicals or atoms. The active particles—ions, atoms and radicals—produced in irradiation enter into secondary processes. This results in a highly complicated nature of a radiation chemical process as a whole.

Let us consider the possible elementary processes that have already been considered in the sections devoted to the laws of decomposition and formation of molecules, photochemistry and chemical reactions in electrical discharges.

If the action of radiation begins with the ionization of molecule A, the process can be depicted as follows:

$$A \rightsquigarrow A^+ + e$$

The wavy arrow indicates the absorption of a definite portion of radiation (similar to the symbol $+ h\nu$ for photochemical processes).

Mass spectrometric investigations show that processes of a single ionization of the initial molecule are the most probable ones.

Further the process of neutralization and the formation of an excited molecule A is possible:

$$A^+ + e \rightarrow A^*$$

Simultaneously with this process, the electron released in ionization may be captured by another molecule M (here M may be a molecule of the same species as A or of a different one):

$$M + e \rightarrow M^-$$

If the ion $A^+$ formed in the initial reaction acquires a more stable configuration, then neutralization may occur by reaction of $A^+$ with the ion of the opposite sign $M^-$:

$$A^+ + M^- \rightarrow A^* + M$$

The excited molecule $A^*$ may decompose into free atoms or radicals R and X or split into smaller stable molecules B and C:

$$A^* \begin{cases} \rightarrow R + X \\ \rightarrow B + C \end{cases}$$

In a liquid phase the second process of reconstruction of the excited molecule is more probable. It results in splitting of the molecule into two stable ones. The ion $A^+$ formed may directly decompose in two ways:

$$A^+ \begin{cases} \rightarrow R^+ + X \\ \rightarrow B^+ + C \end{cases}$$

One of the two possible reactions leads to the formation of a free radical and an ion of a free radical, and the other to the formation of a molecule and a molecular ion. It may be assumed that the first reaction requires a greater dissipation of energy.

It can be seen from the above that the most diverse processes are possible under the action of radiation, especially if organic molecules participate in the reactions.

The free radicals and atoms formed may initiate chain processes. For example, the following processes are possible in polymerization:

$$R\cdot + A \rightarrow RA\cdot$$
$$RA\cdot + A \rightarrow RA_2\cdot$$
$$\cdots\cdots\cdots$$
$$RA_n\cdot + A \rightarrow RA_{n+1}\cdot$$

Thus irradiation may cause, for example, the polymerization of acrylonitrile in water.

In many polymers, in particular in polyethylene, the number of cross bonds grows under the action of γ-rays. This increases the mechanical strength and thermal stability of the polymer, and also its resistance to the action of solvents. The formation of cross bonds is due to splitting off of the side branches, which leads to the formation of radicals. The latter interact with the adjacent molecules and form chemical bonds with them. Frequently the result of irradiation is rupturing of the main bonds, which leads to a reduction of the average molecular mass. Such a phenomenon is observed in the formation of polyisobutylene.

Interesting results are obtained in the chlorination of hydrocarbons. The chlorination of benzene under the action of γ-rays proceeds in the same way as under the action of ultraviolet light. In toluene, however, the action of ultraviolet light leads to chlorination of the methyl group, while the action of γ-radiation leads to chlorination in the benzene ring. The advantage of γ-rays over ultraviolet ones consists not only in the fact that the former can be used to conduct processes which are impossible with other sources of activation, but also in that γ-rays do not require conducting of the process in glass or quartz apparatus.

**11.8. Influence of Aggregate State.** Reactions in a condensed phase are characterized by a number of specific processes which change the course of a reaction in comparison with that in the gaseous phase. The great increase in density upon transition from the gaseous phase to the liquid one increases the specific ionization, but simultaneously makes deactivation easier and reduces the duration of the excited state. The recombination of ions and radicals is facilitated by the close proximity of molecules of the liquid, which play the part of a third particle. In addition, direct recombination of those parts of a molecule that form as a result of direct dissociation is possible. This phenomenon is also observed in gases with a great molecular mass. The probability of recombination of radicals, excited molecules and ions grows with an increase in the molecular mass of the compounds. The greater the molecule of a gas, the bigger is the number of its degrees of freedom and the longer is the time the molecule can be in a state with a great store of energy owing to the distribution of this energy among the degrees of freedom. In addition, the greater a molecule, the smaller will be the difference between the configuration of an ion and that of an uncharged molecule, and the more probable will be the process of discharge of the ion without following decomposition. Below are given data according to C. Schoepfle and C. Fellows on the amount of gas liberated when various alkanes with a normal structure were irradiated with

electrons having an energy of 170 MeV:

| Alkane | Amount of gas liberated during 30 min, $cm^3$ |
|---|---|
| *n*-Hexane | 57.6 |
| *n*-Heptane | 51.4 |
| *n*-Octane | 48.3 |
| *n*-Decane | 41.6 |
| *n*-Tetradecane | 34.9 |

It is quite obvious that an increase in the molecular mass of the alkane is accompanied by a reduction in the amount of gas formed.

In solutions and polar liquids the solvation effect violates the stability of the ions formed and the probability of their conversion into radicals. Thus the reason for the essential difference between the radiation chemical activity of a given substance in the liquid and the gaseous states should be sought not in the difference between the primary physical processes, but in a change in the probability of the secondary processes that proceed after the primary acts of excitation and ionization.

**11.9. Radiolysis of Water.** The radiolysis of water and aqueous solutions of many substances is of special interest. The following summary reactions take place upon irradiation of water:

$$2H_2O \longrightarrow H_2O_2 + H_2$$

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

The yield of hydrogen peroxide under the action of x-rays, $\gamma$-rays and $\beta$-rays is considerable only if the water contains dissolved oxygen. In the absence of oxygen these reactions proceed with a very low yield. In radiolysis with $\alpha$-particles the yield of hydrogen peroxide is the same in water saturated with oxygen and entirely free of it.

The primary chemical action of radiation leads to the formation of the radicals H and OH· as follows:

$$H_2O \rightsquigarrow H_2O^+ + e$$

$$H_2O^+ + aq \longrightarrow H^+aq + OH\cdot$$

$$e + H_2O + aq \longrightarrow OH^-aq + H$$

$$H^+aq + OH^-aq \longrightarrow H_2O$$

$$\overline{H_2O \rightsquigarrow OH\cdot + H}$$

The distribution of these radicals in space immediately after their formation depends on the kind o initiating radiation. In the passage of $\alpha$-particles, low-energy protons and low-energy electrons, great concentrations of radicals are formed along the tracks of the particles. These radicals react with one another, which leads

to the formation of hydrogen, hydrogen peroxide and water as follows:

$$H + H \rightarrow H_2$$

$$OH\cdot + OH\cdot \rightarrow H_2O_2$$

$$H + OH\cdot \rightarrow H_2O$$

It can thus be considered that two reactions occur under the action of radiation

$$2H_2O \longrightarrow H_2O_2 + H_2$$

$$H_2O \longrightarrow H + OH\cdot$$

Similar reactions proceed in water containing dissolved oxygen under the action of $\gamma$-radiation. If the water contains no dissolved oxygen, these reactions are almost unnoticeable.

In pure water, containing no solutes, the following reactions also proceed

$$H + H_2O_2 \rightarrow H_2O + OH\cdot$$

$$OH\cdot + H_2 \rightarrow H_2O + H$$

These reactions can be considered as reverse chain reactions leading to the destruction of the products of decomposition of the water. Another reaction is possible for the hydrogen peroxide that inhibits its decomposition:

$$H_2O_2 + OH\cdot \rightarrow H_2O + HO_2\cdot$$

$$HO_2\cdot + H \rightarrow H_2O_2$$

The radicals appearing as a result of the reaction are capable of reacting with the solutes.

Many substances added to water may inhibit reverse reactions, since they cause recombination of the radicals. The solutes are frequently either oxidized or reduced, reacting with the hydroxyl radicals, hydrogen atoms and hydrogen peroxide molecules. For example, the following reactions may occur in the presence of bromide ions:

$$Br^- + OH\cdot \rightarrow Br + OH^-$$

$$Br + H \rightarrow Br^- + H^+$$

The presence of oxygen in the solution leads to the formation of free radicals $HO_2\cdot$ according to the reaction

$$H + O_2 \rightarrow HO_2\cdot$$

These radicals on one hand react with hydrogen peroxide and hydroxyl, oxygen being formed according to the reactions

$$H_2O_2 + HO_2\cdot \rightarrow H_2O + OH\cdot + O_2$$

$$OH\cdot + HO_2\cdot \rightarrow H_2O + O_2$$

On the other hand they participate in reactions of formation of

hydrogen peroxide as follows:

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$$
$$H + HO_2\cdot \rightarrow H_2O_2$$

It is according to these reactions that hydrogen peroxide is formed under the action of $\gamma$-radiation on water containing dissolved oxygen.

**11.10. Radiolysis of Aqueous Solutions.** As indicated above, the oxidation and reduction reactions proceeding in the aqueous solutions of many substances upon irradiation can be explained by the formation of the radicals H, OH· and $HO_2\cdot$. For example, upon irradiation of acid solutions of ferrous sulphate in the absence of oxygen, the following reaction proceeds:

$$Fe^{2+} + OH\cdot \rightarrow Fe^{3+} + OH^-$$

In a solution saturated with air, the radicals $HO_2\cdot$ form and react with the ions of the bivalent iron as follows:

$$Fe^{2+} + HO_2\cdot \rightarrow HO_2^-\cdot + Fe^{3+}$$

In addition, the hydrogen peroxide formed may also serve as the oxidizer.

A solution of potassium bichromate in an acid medium is reduced under the action of x-rays and $\gamma$-rays. Solutions of $KIO_3$ are reduced and benzene is oxidized to phenol upon irradiation with $\alpha$-rays and x-rays. Irradiation of aqueous solutions of benzene in the absence of oxygen leads to the formation of phenol and diphenyl as follows:

$$C_6H_6 + OH\cdot \rightarrow C_6H_5\cdot + H_2O$$
$$C_6H_5\cdot + OH\cdot \rightarrow C_6H_5OH$$
$$C_6H_5\cdot + C_6H_5\cdot \rightarrow C_6H_5-C_6H_5$$

If oxygen is dissolved in the water, the yield of phenol grows several times. This can be explained by the fact that the oxygen forming radicals $HO_2\cdot$ in the water removes hydrogen atoms from the reaction mixture. It thus inhibits the recombination of the atomic hydrogen with the free hydroxyl and the phenyl radicals, which would lead to the formation of water and benzene. In addition, the radical $HO_2\cdot$ interacts with the free phenol to form phenol hydroperoxide, the latter decomposing to form phenol.

Of great interest is the phenomenon of one solute preventing the decomposition of another one under the action of radiation. For example, the action of x-rays on aqueous solutions of acetone causes decomposition of the latter, but the addition of formic acid in an amount not less than 10% of the amount of acetone practically completely protects the latter from decomposition by the x-rays.

**11.11. Ionic and Radiation Chemical Yields.** The measure or efficiency of energy absorption in radiolysis i $G$, the total number

of molecules converted per 100 eV of radiation energy absorbed, or the number of electron-volts causing the transformation of one molecule of the substance, i.e. the quantity $100/G$. The quantity $G$ is called the *radiation chemical yield.*

To characterize a process proceeding under the action of radiation, the concept *ionic yield* is sometimes used in radiation chemistry. By ionic yield is meant the ratio of the number of molecules transformed upon irradiation to the number of ion pairs formed upon absorption of the same dose of radiation. The concept is applicable only to such reactions in the gaseous phase for which the number of ion pairs formed can be determined. The concept is not applicable to reactions in condensed phases, where it is impossible to determine the number of ion pairs formed. Ionic yield does not take into account the appreciable part played by the atoms, radicals and excited molecules appearing under the action of radiation.

**11.12*. Kinetics of Radiolysis of Solutions.** The kinetics of reactions of radiolysis in dilute aqueous solutions can frequently be described by the simple equation

$$\frac{dn}{dt} = k_1 p - k_2 nc - (k_3 + k_4)\, n^2 \tag{11.2}$$

where $dn/dt$ = change in concentration of radicals with time
$p$ = power of absorbed radiation dose
$c$ = concentration of solute
$k_1$ = number of radicals formed related to a unit of dose except for the radicals that cannot leave the region of their generation; these radicals do not encounter solute molecules and, consequently, do not participate in reactions of solute transformation during irradiation
$k_2$ = rate constant of reaction of removing radicals by their interaction with the solute
$k_3$ = rate constant of recombination of radicals by collisions with molecules of the liquid
$k_4$ = rate constant of reaction between radicals.

While the value of $c$ is constant throughout the entire volume of the system, the number $n$ of radicals in one cubic centimetre is never the same owing to the loss of energy ionizing the particles along a track. The nature and degree of this variation should be taken into account when considering Eq. (11.2), which obviously only gives a qualitative characteristic of a process.

The rate of a chemical reaction is characterized by the rate of disappearance of the solute, for which we can write

$$-\frac{dc}{dt} = k_2 Pnc \tag{11.3}$$

where $P$ is the probability of the fact that upon the disappearance of a radical as a result of reaction with a dissolved molecule the latter will change chemically.

The concentration of the radicals in Eq. (11.3) can be found for a stationary state, when

$$\frac{dn}{dt} = 0 \tag{11.4}$$

or

$$k_1p - k_2nc - (k_3 + k_4)\, n^2 = 0 \tag{11.5}$$

If

$$k_2c \gg (k_3 + k_4)\, n \tag{11.6}$$

the last term in Eq. (11.5) may be neglected, and, therefore,

$$k_1p = k_2nc \tag{11.7}$$

Inserting the found value of $n$ in Eq. (11.3), we get

$$-\frac{dc}{dt} = k_1Pp \tag{11.8}$$

i.e. the rate of change in the concentration of the solute does not depend on its concentration. The differential ionic yield determined by dividing the rate of a reaction by the rate of formation of ion pairs at the given moment depends neither on the concentration of the solute nor on the power of the radiation dose.

If

$$k_2c \ll (k_3 + k_4)\, n \tag{11.9}$$

we may neglect the second addend in Eq. (11.5). Hence

$$k_1p = (k_3 + k_4)\, n^2 \tag{11.10}$$

whence

$$n = \left(\frac{k_1p}{k_3 + k_4}\right)^{1/2} \tag{11.11}$$

Inserting Eq. (11.11) into Eq. (11.3), we get

$$-\frac{dc}{dt} = k_2Pc\left(\frac{k_1p}{k_3 + k_4}\right)^{1/2} \tag{11.12}$$

i.e. the rate of change in the concentration of the solute is proportional to its concentration and the square root of the power of the dose.

The radicals formed may react not only with the reactants, but also with the products. In this case the kinetic equation (11.3) should be written as follows:

$$\frac{dn}{dt} = k_1p - k_2nc_1 - k_2'nc - (k_3 + k_4)\, n^2 \tag{11.13}$$

where $c_1$ and $c_2$ are the concentrations of the reactant and product, respectively.

If $k_2 \approx k_2'$, Eq. (11.13) can be written as follows:

$$\frac{dn}{dt} = k_1p - k_2nc_0 - (k_3 + k_4)\, n^2 \tag{11.14}$$

where $c_0 = c_1 + c_2$.

When inequality (11.6) holds, then for a stationary state

$$n = \frac{k_1p}{k_2c_0} \tag{11.15}$$

Inserting Eq. (11.15) into Eq. (11.3), we have

$$-\frac{dc}{dt} = k_1Pp\,\frac{c}{c_0} \tag{11.16}$$

Integration of this equation yields

$$c = c_0e^{-k_1Ppt/c_0} \tag{11.17}$$

i.e. the concentration of the solute exponentially decreases with the dose. Such a relation is observed for the reaction of oxidation of hemoglobin to methemoglobin under the action of x-rays.

# CHAPTER 12

# CATALYTIC REACTIONS

**12.1. Classification of Chemical Processes. Catalysis.** Most chemical processes are activated ones, i.e. they proceed through an activated complex whose composition, structure and properties determine the kinetic properties of the system—the rate of the reaction, its direction, the influence of external factors on it, etc. In the previous chapters we considered cases when the composition of the activated complex included only molecules of the reactants. There is a very great group of reactions, however, in which the activated complex includes substances that stoichiometrically are not participants of the reaction. The process of decomposition of the intermediate yields the products, while the foreign substance included in the composition of the intermediate is regenerated. By the end of the reaction this substance is found to be unchanged both in its chemical composition and quantitatively; sometimes only physical changes are possible. Two main kinds of such phenomena are known:

1. The reactants and the additional component of the activated complex are in the same phase, for example the gaseous or condensed one.

2. The reactants and the additional component are in different phases, and the activated complex is formed on the phase interface.

The phenomenon when the composition of the activated complex includes a substance that does not participate stoichiometrically in the summary process, but changes the kinetic properties of the system, is called *catalysis*, and the additional component itself is called a *catalyst*.

On the basis of the above, all chemical processes with thermal excitation, depending on the composition of the activated complex, can be classified as follows.

1. *Homogeneous non-catalytic processes*—the activated complex consists of the initial molecules of the reactants or of intermediates formed from the reactants.

2. *Homogeneous catalytic processes*—in addition to the initial molecules, the activated complex consists of a substance that is in the same phase as the reacting molecules, but does not enter into the stoichiometric equation of the reaction.

3. *Heterogeneous catalytic processes*—in addition to the initial molecules, the activated complex consists of a substance that is in a different phase than the reacting molecules and does not enter into the stoichiometric equation of the reaction. The activated complex, as a rule, is formed on the phase interface, frequently being a surface system of the chemisorption type.

In catalytic reactions, especially homogeneous ones, the composition of the activated complex sometimes includes one of the reactants or one of the products, and therefore the concentration of the catalyst changes in the course of the reaction. Such processes have been called *autocatalytic* ones[1].

Catalytic phenomena are complicated and diverse. For this reason the general definitions require clarification and detailization.

Since the concentration of the activated complex is only a small fraction of that of the reactants, even a negligible amount of catalyst often changes the kinetic properties of a system. For example, to appreciably change the rate of oxidation of sodium sulphite in an aqueous solution, it is sufficient to introduce $10^{-13}$ g-equiv. of a catalyst (copper sulphate) into one litre of the solution.

Different catalysts may form activated complexes of one type or having different structures with the same reactants. In the latter case the difference in the configurations of the activated complex may lead to a change in the direction of the process, and different products may be formed from the same reactants. The property of catalysts to change the direction of a process is called *selectivity*. It especially clearly manifests itself, as will be shown below, in heterogeneous systems.

As noted above, by the invariability of a catalyst in a process is meant the constancy of its amount and chemical composition before and after the reaction. The physical state of a catalyst entering the composition of an activated complex may appreciably change. For example, coarse crystals of manganese dioxide catalyzing the decomposition of potassium chlorate are converted into a fine crystalline powder in the course of the reaction. Cases are known when after long contact the state of the surface layers of a solid—a heterogeneous catalyst—appreciably changed.

The rate of a catalytic reaction may be greater or smaller than that of a non-catalytic one, i.e. the catalyst in the composition of the activated complex may either accelerate a reaction—*positive catalysis*, or inhibit it—*negative catalysis*. Such a comparison is not always possible practically, however, since some processes do not

[1] For a complete generalization this classification should be supplemented with cases of specific (not thermal) methods of activating the initial molecules, i.e. with photochemical and electrochemical reactions, and with reactions proceeding under the action of an electric discharge or radiation.

proceed at all without a catalyst, the reactants reacting in a different direction[1].

It does not at all follow from the above that a catalyst may bring about a process which is thermodynamically impossible. Since the catalyst enters the composition of only the intermediate, the thermodynamic possibility of a process is determined by the difference between the levels of the free energy in the final and initial states. Thus, in the presence of a catalyst a chemical process also proceeds in the direction of a minimum of free energy in the system, and the catalyst only accelerates (or inhibits) this process, i.e. is not capable of shifting the position of equilibrium. The same conclusion can be reached by considering the following model. Let us imagine an isothermal system consisting of gaseous components in which a reaction with a change in the number of moles is thermodynamically possible. Let us assume that there is a catalyst shifting the position of equilibrium. It would now be possible, by alternately introducing the catalyst into the system and removing it, to obtain work of expansion and compression of the gases in the absence of a temperature difference without any limit. Consequently, the assumption made on the possibility of the shifting of equilibrium in the presence of a catalyst leads to the possibility of constructing a perpetuum mobile of the second kind, i.e. to violation of the second law of thermodynamics.

This general rule on the impossibility of shifting equilibrium in the presence of a catalyst is true with one reservation, namely, if as a result of a reaction the physical state of the catalyst sharply changes, equilibrium may shift by an amount corresponding to the change in the free energy. As a rule this effect is so small that it has no practical significance.

Catalysis is of tremendous importance in engineering and in nature. By selecting appropriate catalysts, processes can be conducted in the desired direction and at the required rate. The field of application of catalytic reactions in the chemical industry at present is absolutely boundless. We shall only note that such important processes as the production of sulphuric acid, the synthesis of ammonia, the oxidation of ammonia to nitric acid and many others are catalytic ones.

It can be asserted that without catalysis life in general would be impossible. It is sufficient to say that the process of assimilation of carbon dioxide by the chlorophyll of plants underlying vital activity is a photochemical and catalytic process. The simplest organic substances formed as a result of assimilation then undergo a number of complicated transformations. The chemical functions of living cells include the decomposition and synthesis of proteins, fats, carbohydrates, the synthesis of various molecules, frequently of a quite complicated nature. Thus, a cell is a peculiar and quite perfect chemical laboratory, and if we take into account that all these processes are catalytic ones—a catalytic laboratory. Biological processes are catalyzed by special substances called *ferments*. If we

[1] This is why the definitions of catalysis based on a comparison of the rates of a catalytic and non-catalytic reactions are not general.

compare the inorganic catalysts that we know with ferments, we are struck first of all by the tremendous catalytic activity of the latter. Thus, one mole of the ferment alcohol dehydrogenase at room temperature during one second converts 720 moles of alcohol into acetic aldehyde, while industrial catalysts of the same process (in particular copper) at 200 °C during one second convert not over 0.1-1 mole per gramme-atom of catalyst. Or, for example, one mole of the ferment catalase at 0 °C decomposes 200 000 moles of hydrogen peroxide a second. The most active inorganic catalysts (platinum black) at 20 °C decompose 10-80 moles of hydrogen peroxide a second on one gramme-atom of the catalyst. These examples show that the activity of natural biological catalysts is many times greater than that of synthetic inorganic catalysts. It is the highly specific nature and directed action of a ferment, and also its ability to process an enormous number of substrate molecules during a short time at the temperature of the living organism that allow ferments to produce compounds essential for the vital activity, or to destroy useless, and sometimes harmful, substances accumulating in the organism in the process of its vital activity.

It is clear from the above how important it is to know the structure and mechanism of action of biological catalysts. These problems are studied by a branch of science called *biocatalysis*. A knowledge of the mechanism of ferment action makes it possible, by modelling biological systems, to improve ordinary inorganic catalysts. In addition, the catalytic activity of ferments is widely used in industry in various fermentation processes.

## *Homogeneous Catalytic Reactions*

**12.2. General Kinetic Laws.** Many reactions in the gaseous phase are of a distinct catalytic nature. These include, in particular, processes in which molecular iodine is the catalyst. For example, the monomolecular non-catalytic pyrolysis of diethyl ether results in the formation of methane, ethylene and carbon monoxide:

$$C_2H_5OC_2H_5 \rightleftarrows 2CH_4 + \frac{1}{2}C_2H_4 + CO$$

In the presence of iodine the rate of decomposition of the ether increases about 10 000 times, the result being the formation of ethane, methane and carbon monoxide:

$$C_2H_5OC_2H_5 \rightleftarrows C_2H_6 + CH_4 + CO$$

i.e. the catalyst leads to a change not only in the rate, but also in the direction of the process. Here this is due to a change in the mechanism of the reaction. The primary process consists in the splitting of a molecule of the ether by the action of the iodine and the formation of the intermediates ethyl iodine, hydrogen iodide and acetic aldehyde:

$$C_2H_5OC_2H_5 + I_2 \rightarrow C_2H_5I + HI + C_2H_4O$$

The secondary processes leading to the formation of the products consist in the formation of ethane with the regeneration of the catalyst

$$C_2H_5I + HI \rightarrow C_2H_6 + I_2$$

and in the decomposition of the acetic aldehyde

$$C_2H_4O \rightarrow CH_4 + CO$$

In comparison with the non-catalytic reaction ($E$ = 51 800 cal/mol) the activation energy of this catalytic reaction decreases by 17 800 cal/mol. If we assume that the values of the preexponential factors are close to each other for reactions in a gaseous phase in the same conditions, we get the following ratio of the rates of the two reactions:

$$\frac{\text{Rate of catalytic reaction}}{\text{Rate of non-catalytic reaction}} = \frac{e^{-34\,000/RT}}{e^{-51\,800/RT}} = e^{-17\,800/RT}$$

At 700 K this ratio is $3.45 \times 10^5$, which is about thirty times greater than the experimental result. This is explained by the approximate nature of the assumption that the preexponential factors are equal. Since in the example being considered the direction of the reaction changes, a change in the numerical value of the preexponential factor should also be expected for various reasons (the stereometry of the collisions, a change in the number of effective degrees of freedom and, finally, a change in the effective diameter of collision). This explains the discrepancy between the calculated and experimental data.

TABLE 12.1

**Selected Catalytic Reactions in the Gaseous Phase (Catalyst — Molecular Iodine)**

| Decomposing molecule | Activation energy, cal/mol | | $\Delta E = E_1 - E_2$, cal/mol | Acceleration at 700 K | |
|---|---|---|---|---|---|
| | for non-catalytic reaction, $E_1$ | for catalytic reaction, $E_2$ | | calculated $e^{\Delta E/RT}$ | obtained experimentally |
| $CH_3OC_2H_5$ | 46 000 | 38 000 | 8 000 | $3.17 \times 10^2$ | $10^2$ |
| $C_2H_5OC_2H_5$ | 51 800 | 34 000 | 17 800 | $3.45 \times 10^5$ | $10^4$ |
| $C_3H_7OC_3H_7$ | 60 500 | 28 500 | 22 000 | $6.94 \times 10^6$ | $10^5$ |
| $CH_3CHO$ | 45 500 | 32 500 | 13 000 | $1.14 \times 10^4$ | $10^4$ |

Table 12.1 summarizes the comparative data on the kinetics of reactions accelerated by molecular iodine. The mechanism of these reactions is similar to that of the decomposition of diethyl ether. The change in the direction of the process in the presence of the catalyst is characteristic of all cases. If we limit ourselves to consideration of the data for the decomposition of the three ethers, the following regularity is evident: for non-catalytic reactions the

activation energy increases for more complicated molecules, and for catalytic ones it decreases. The acceleration, as can be seen from the last two columns of the table, is mainly due to the reduction of the activation energy in the presence of the catalyst. The preexponential factors grow not more than 70 times. This effect apparently also grows as the molecules of the decomposing substance become more complicated.

Homogeneous catalytic reactions are characteristic of the processes conducted in the liquid phase. These processes include the esterification and hydrolysis of esters, the inversion of sugars and the mutarotation of glucose accelerated by the action of hydrogen ions, and also the decomposition of hydrogen peroxide in aqueous solutions catalyzed by certain anions and cations. They also include the polymerization of olefins in the liquid phase under the action of sulphuric acid, the polymerization of olefins in the liquid and vapour phases in the presence of boron trifluoride or hydrogen fluoride and many others.

In all these processes, as in those considered above, the part played by the catalyst formally consists in a reduction of the activation energy and, consequently, in acceleration of the reaction. In addition, the participation of a catalyst in a process leads to a more complicated kinetic law of the reaction and to the appearance of new kinetic equations not known in non-catalytic kinetics. Let us consider as an example a bimolecular non-catalytic reaction:

$$A + B \rightarrow AB^{*} \rightarrow \text{Products}$$

In the presence of a catalyst C, which participates in the formation of the activated complex, the first step—the formation of the intermediate, proceeds as follows:

$$A+B+C \underset{k_2}{\overset{k_1}{\rightleftarrows}} ABC^{*}$$

In accordance with the activated complex theory, we consider that equilibrium exists between the reactants and the activated complex. This assumption, as will be shown below, is not obligatory, but determines the kind of kinetic equation obtained. Consequently, its correctness in specific cases can be verified experimentally. The rate of a process as a whole is determined by the rate of decomposition of the activated complex in the direction of formation of the products and regeneration of the catalyst:

$$ABC^{*} \xrightarrow{k_3} C+\text{Products}$$

From the condition of equilibrium of the first step we have

$$k_1 [A] [B] \{[C] - [ABC^{*}]\} = k_2 [ABC^{*}] \qquad (12.1)$$

where $\{[C]-[ABC^{*}]\}$ is the amount of catalyst in the free state.

From Eq. (12.1) we find the concentration of the activated complex:

$$[ABC^*] = \frac{k_1 [A] [B] [C]}{k_2 + k_1 [A] [B]} \tag{12.2}$$

Consequently, the rate of the process as a whole is described by the equation

$$-\frac{d[A]}{dt} = k_3 [ABC^*] = \frac{k_3 k_1 [A] [B]}{k_2 + k_1 [A] [B]} [C] \tag{12.3}$$

In particular cases Eq. (12.3) can have a simpler form. Thus, if equilibrium between the reactants and the activated complex is shifted toward the latter, i.e. $k_1 \gg k_2$, then we also have $k_1 [A] [B] \gg k_2$. Here Eq. (12.3) yields

$$-\frac{d[A]}{dt} \approx k_3 [C] \tag{12.4}$$

If equilibrium is shifted toward the reactants, then $k_2 \gg k_1 [A] [B]$ and Eq. (12.3) becomes

$$-\frac{d[A]}{dt} = \frac{k_3 k_1}{k_2} [A] [B] [C] \tag{12.5}$$

It follows from Eqs. (12.3) to (12.5) that whatever the form of the kinetic law, the rate of a process is always directly proportional to the concentration of the catalyst. The validity of this rule is completely confirmed by experiments. The only exception here is a great excess of the catalyst, as a result of which not kinetic, but purely physical laws (for example, diffusion of the solute to the catalyst) may limit the rate of a process. Figure 12.1 shows the paths of the reaction considered above according to a non-catalytic and a catalytic mechanisms. It can be seen that the difference in the activation energies is the enthalpy of formation of the activated complex including the catalyst from the activated complex consisting only of the reactants. This figure also illustrates the case when catalyst $C_2$ initiates a process that in general

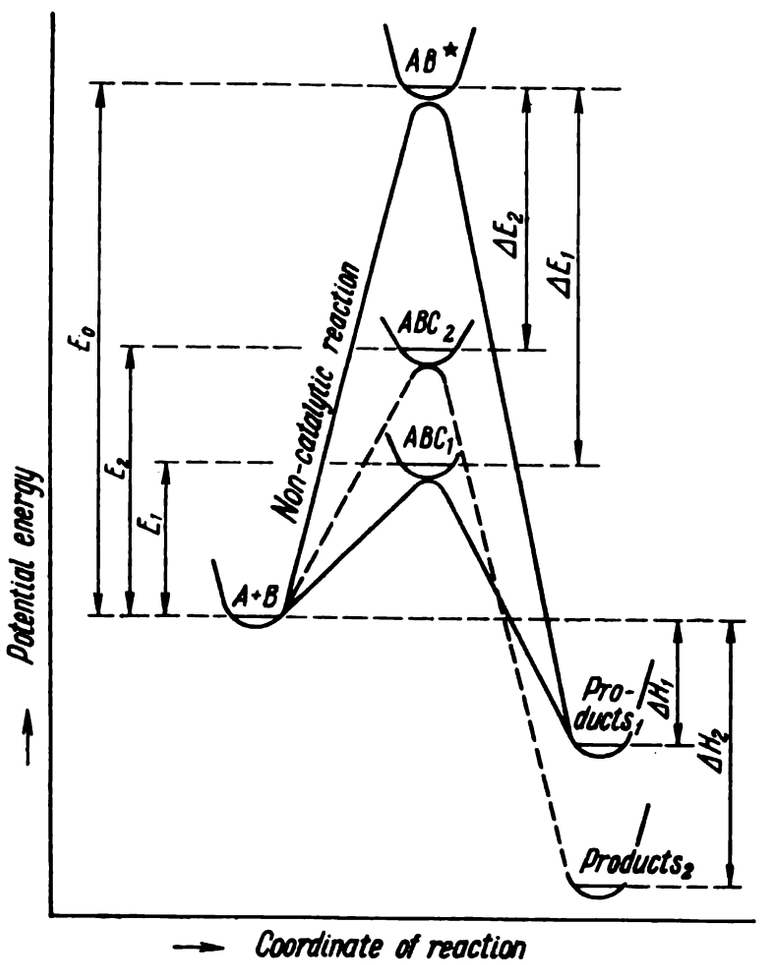



Fig. 12.1. Curves of potential energy along reaction coordinate for a non-catalytic and a homogeneous catalytic processes

does not proceed without its participation and that leads to the formation of other products in comparison with the result of the action of catalyst $C_1$ and that of the non-catalytic reaction. Experiments give many examples of such selective action of catalysts. For example, the oxidation of thiosulphate ions by hydrogen peroxide in an aqueous solution in the presence of iodide ions is described by the following stoichiometric equation:

$$2S_2O_3^{2-} + H_2O_2 + 2H^+ = S_4O_6^{2-} + 2H_2O$$

If molybdenic acid is used as the catalyst, the direction of the reaction will change and the products will be sulphate ions and water:

$$S_2O_3^{2-} + 4H_2O_2 = 2SO_4^{2-} + 2H^+ + 3H_2O$$

Here also the change in the direction of the reaction is due to a change in the nature of the composition and structure of the activated complex. In the first case the reaction proceeds in three steps with the formation of two intermediates $IO^-$ and $I_2$ as follows:

1. Interaction of one of the reactants with the catalyst leads to the formation of the first intermediate:

$$I^- + H_2O_2 \rightarrow IO^- + H_2O$$

2. Interaction of the first intermediate with the catalyst leads to the formation of the second intermediate:

$$I^- + IO^- + 2H^+ \rightarrow I_2 + H_2O$$

3. Interaction of the second reactant with the activated complex leads to the formation of the products and regeneration of the catalyst:

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$$

In the second case the permolybdate ion is the activated complex, and the reaction proceeds as follows:

1. Formation of the activated complex

$$MoO_4^{2-} + 4H_2O_2 \longrightarrow MoO_8^{2-} + 4H_2O$$

2. Formation of the product and regeneration of the catalyst

$$MoO_8^{2-} + S_2O_3^{2-} + H_2O \longrightarrow 2SO_4^{2-} + 2H^+ + MoO_4^{2-}$$

Equation (12.3) was deduced on the assumption that the reactants and the activated complex were in equilibrium. Now let us consider the deduction of a kinetic equation without this assumption. Let us also change the presumed mechanism, considering that the activated complex is formed when the catalyst reacts only with one of the reactants, i.e. the reaction without a catalyst proceeds as follows

$$A + B \rightarrow AB^* \rightarrow \text{Products}$$

and with the catalyst C its mechanism is

$$A + C \xrightarrow{k_1} AC^*$$

$$AC^* + B \xrightarrow{k_3} C + \text{Products}$$

In the given case the condition of equilibrium is replaced by the condition of a stationary state:

$$\frac{d[AC^*]}{dt} = k_1[A]\{[C]-[AC^*]\} - k_3[B][AC^*] = 0 \tag{12.6}$$

from which we get

$$[AC^*] = \frac{k_1[A][C]}{k_1[A]+k_3[B]} \tag{12.7}$$

Taking into account that

$$-\frac{d[A]}{dt} = k_3[B][AC^*] \tag{12.8}$$

we obtain the following expression for the rate of the reaction:

$$-\frac{d[A]}{dt} = \frac{k_3k_1[A][B]}{k_1[A]+k_3[B]}[C] \tag{12.9}$$

Here also the limit forms of the kinetic equation have a definite practical significance. They follow from the conditions that when $k_1[A] \gg k_3[B]$ we have

$$-\frac{d[A]}{dt} \approx k_3[B][C] \tag{12.10}$$

and when $k_3[B] \gg k_1[A]$ we have

$$-\frac{d[A]}{dt} \approx k_1[A][C] \tag{12.11}$$

Table 12.2 gives different forms of the kinetic equations for monomolecular and bimolecular (relative to the reactants) homogeneous catalytic reactions. It can be seen from the relations given in the table that the rule of direct proportionality between the reaction rate and the catalyst concentration is obeyed in all cases regardless of the mechanism of formation of the activated complex. The kinetic law in the general case, however, depends on the accepted mechanism of formation of the activated complex and its composition. The only exception are two mechanisms of formation of the activated complex in a monomolecular (relative to the reactants) catalytic reaction, which are kinetically indistinguishable in pairs. It follows that the establishment of a kinetic law on the basis of experimental data frequently makes it possible to reveal the mechanism of the reaction and determine the composition of the activated complex Methods of practical application of the equations given above will be considered later.

**12.3. Homogeneous Decomposition of Hydrogen Peroxide.** The catalytic decomposition of hydrogen peroxide in an aqueous solution is accelerated by many ions, for example $Cr_2O_7^{2-}$, $WO_4^{2-}$, $MoO_4^{2-}$, $Fe^{2+}$ and $Fe^{3+}$. Since this reaction is a model one for determining the activity of certain ferments, in particular catalase, it is frequently called a *catalase process*.

On the basis of this reaction E. Shpitalsky in 1926 formulated the main tenets of the theory of homogeneous catalysis. N. Kobozev together with his co-workers, beginning from 1931, succeeded in separating in the pure state a number of intermediates of this reaction and studying their kinetic properties.

TABLE 12.2

**Typical Forms of Kinetic Equations for Selected Homogeneous Catalytic Reactions**

| Mechanism | Kinetic equation | Limit conditions | |
|---|---|---|---|
| | $A + B \rightarrow$ Products | | |
| $A + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} AC^*$<br>$AC^* + B \xrightarrow{k_3} C + AB$ | $-\frac{d[A]}{dt} = \frac{k_3 k_1 [A][B]}{k_2 + k_1 [A]}[C]$ | $k_1 [A] \gg k_2$<br>$-\frac{d[A]}{dt} \approx k_3 [B][C]$ | $k_2 \gg k_1 [A]$<br>$-\frac{d[A]}{dt} \approx \frac{k_3 k_1}{k_2}[A][B][C]$ |
| $A + B + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} ABC^*$<br>$ABC^* \xrightarrow{k_3} C + AB$ | $-\frac{d[A]}{dt} = \frac{k_3 k_1 [A][B]}{k_2 + k_1 [A][B]}[C]$ | $k_1 [A][B] \gg k_2$<br>$-\frac{d[A]}{dt} \approx k_3 [C]$ | $k_2 \gg k_1 [A][B]$<br>$-\frac{d[A]}{dt} \approx \frac{k_3 k_1}{k_2}[A][B][C]$ |
| $A + C \xrightarrow{k_1} AC^*$<br>$AC^* + B \xrightarrow{k_3} C + AB$ | $-\frac{d[A]}{dt} = \frac{k_3 k_1 [A][B]}{k_1 [A] + k_3 [B]}[C]$ | $k_1 [A] \gg k_3 [B]$<br>$-\frac{d[A]}{dt} \approx k_3 [B][C]$ | $k_3 [B] \gg k_1 [A]$<br>$-\frac{d[A]}{dt} \approx k_1 [A][C]$ |

| | | | |
|---|---|---|---|
| $A+B+C \xrightarrow{k_1} ABC^{\star}$<br>$ABC^{\star} \xrightarrow{k_3} C+AB$ | $-\frac{d[A]}{dt} = \frac{k_3 k_1 [A][B]}{k_3 + k_1 [A][B]}[C]$ | $k_1 [A][B] \gg k_3$<br>$-\frac{d[A]}{dt} \approx k_3 [C]$ | $k_3 \gg k_1 [A][B]$<br>$-\frac{d[A]}{dt} \approx k_1 [A][B][C]$ |
| $AB \longrightarrow$ Products | | | |
| $AB+C \underset{k_2}{\overset{k_1}{\rightleftarrows}} AC^{\star}+B$<br>$AC^{\star} \xrightarrow{k_3} C+A$<br>$AB+C \underset{k_2}{\overset{k_1}{\rightleftarrows}} ABC^{\star}$<br>$ABC^{\star} \xrightarrow{k_3} A+B+C$ | $-\frac{d[A]}{dt} = \frac{k_3 k_1 [AB]}{k_2 [B] + k_1 [AB]}[C]$ | $k_1 [AB] \gg k_2 [B]$<br>$-\frac{d[A]}{dt} \approx k_3 [C]$ | $k_2 [B] \gg k_1 [AB]$<br>$-\frac{d[A]}{dt} \approx \frac{k_3 k_1}{k_2}\frac{[AB]}{[B]}[C]$ |
| $AB+C \xrightarrow{k_1} AC^{\star}+B$<br>$AC^{\star} \xrightarrow{k_3} C+A$<br>$AB+C \xrightarrow{k_1} ABC^{\star}$<br>$ABC^{\star} \xrightarrow{k_3} A+B+C$ | $-\frac{d[AB]}{dt} = \frac{k_3 k_1 [AB]}{k_3 + k_1 [AB]}[C]$ | $k_1 [AB] \gg k_3$ .<br>$-\frac{d[A]}{dt} \approx k_3 [C]$ | $k_3 \gg k_1 [AB]$<br>$-\frac{d[A]}{dt} \approx k_1 [AB][C]$ |

The following are the main tenets of the theory (according to Shpitalsky):

1. A catalyst is such a substance that transforms a reactant into a reactive state, the latter being an unstable activated complex.
2. The formation of an intermediate is a reversible and relatively rapid process.
3. The unstable activated complex decomposes relatively slowly with formation of the products and regeneration of the catalyst.
4. The total rate of the process is proportional to the concentration of the activated complex.

If the formation of an intermediate is expressed by the equation

$$nA + C \rightleftarrows M$$

where A is a molecule of the reactant, C a molecule of the catalyst and M a molecule of the intermediate, then the constant of equilibrium between the reactant and intermediate is

$$K = \frac{[M]}{[A]^n \{[C]_0 - [M]\}} \tag{12.12}$$

where $[C]_0$ is the initial concentration of the catalyst.

Hence

$$[M] = \frac{K[A]^n [C]_0}{1 + K[A]^n} \tag{12.13}$$

Since the total rate of the process as a whole is determined by the rate of decomposition of the intermediate

$$M \xrightarrow{k} \text{Products} + C$$

we have

$$-\frac{d[A]}{dt} = k[M] = \frac{kK[A]^n [C]_0}{1 + K[A]^n} \tag{12.14}$$

Thus, firstly, the rate of the reaction is directly proportional to the concentration of the catalyst, and, secondly, the equation kinetically gives a fractional order of the process between zero and $n$. Indeed, if $K[A]^n \gg 1$ (equilibrium is shifted toward the formation of the intermediate), the formal order with respect to the reactant is equal to the zero one:

$$-\frac{d[A]}{dt} = k[C]_0 \tag{12.15}$$

If $K[A]^n \ll 1$ (equilibrium is shifted toward the reactants), then

$$-\frac{d[A]}{dt} = kK[A]^n [C]_0 \tag{12.16}$$

i.e. the order of the reaction with respect to the reactant will be equal to $n$.

The truth of this theory was verified in the greatest detail by Kobozev on the example of decomposition of $H_2O_2$ in the presence of $MoO_4^{2-}$. He succeeded in separating two intermediates and studying the kinetic properties of each of them. First of all the yellow permolybdate $Na_2MoO_6$

$$2H_2O_2 + MoO_4^{2-} \rightleftarrows MoO_6^{2-} + 2H_2O$$

and the red permolybdate $Na_2MoO_8$

$$4H_2O_2 + MoO_4^{2-} \rightleftarrows MoO_8^{2-} + 4H_2O$$

were identified.

Both permolybdates are kinetically unstable, the rate of decomposition of the red permolybdate according to the equation

$$MoO_8^{2-} \longrightarrow MoO_4^{2-} + 2O_2$$

being 4.5 times greater than that of decomposition of the yellow permolybdate according to the equation

$$MoO_6^{2-} \longrightarrow MoO_4^{2-} + O_2$$

Further investigation has shown that this comparatively simple scheme is made more complicated by two additional circumstances. Firstly, the red permolybdate undergoes partial side decomposition into the yellow one, i.e.

$$MoO_8^{2-} \longrightarrow MoO_6^{2-} + O_2$$

and, secondly, the yellow permolybdate interacts with the catalyst to give another intermediate, i.e.

$$MoO_6^{2-} + MoO_4^{2-} \longrightarrow 2MoO_5^{2-}$$

which kinetically is sufficiently stable.

Similar relations were also found for other catalysts (Table 12.3).

TABLE 12.3

**Intermediates of Homogeneous Catalytic Decomposition of Hydrogen Peroxide**

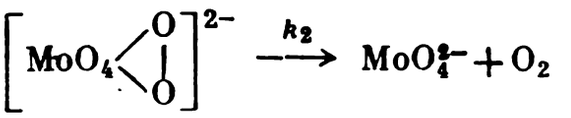
| Catalyst | Intermediates | |
|---|---|---|
| | active form | inactive form |
| $MoO_4^{2-}$ | $MoO_8^{2-}$, $MoO_6^{2-}$ | $MoO_5^{2-}$ |
| $WO_4^{2-}$ | $WO_8^{2-}$ | $WO_5^{2-}$ |
| $Cr_2O_7^{2-}$ | $Cr_2O_9^{2-}$ | Not discovered |
| $Fe^{3+}$ | $Fe_2O_5$ | $Fe_2O_3$ |

In all the examples, except for the one with the ion of trivalent iron, attention is drawn to the fact that the active intermediates contain an even number of excess atoms of oxygen in comparison with the catalyst, and the inactive ones—

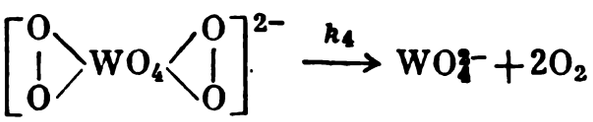
an odd number (one). The explanation is that an intermediate having one excess atom can decompose only according to a bimolecular mechanism, for example

$$MoO_5^{2-} + MoO_5^{2-} \longrightarrow 2MoO_4^{2-} + O_2$$

while for intermediates containing an even number of oxygen atoms the possibility of intramolecular recombination according to a monomolecular path is kinetically more probable, for example



or



It is clear from the above that in real systems several simultaneously functioning active intermediates are formed. In the example of the decomposition of hydrogen peroxide, compounds of the peroxide type containing an even number of excess atoms of oxygen are active forms, and the compound containing one excess atom of oxygen is an inactive form. Compounds containing an odd number of excess atoms of oxygen greater than unity usually decompose with the formation of the basic inactive form and do not have an independent kinetic significance.

The first step of such a complicated process consists in the establishment of equilibrium between the reactants and the activated complexes

$$2H_2O_2 + C \underset{}{\overset{K_2}{\rightleftharpoons}} CO_2 + 2H_2O$$

$$4H_2O_2 + C \overset{K_4}{\rightleftharpoons} CO_4 + 4H_2O$$

$$\cdots\cdots\cdots\cdots\cdots$$

$$2(n-1)\,H_2O_2 + C \overset{K_{2(n-1)}}{\rightleftharpoons} CO_{2(n-1)} + 2(n-1)H_2O$$

$$2n\cdot H_2O_2 + C \overset{K_{2n}}{\rightleftharpoons} CO_{2n} + 2n\cdot H_2O$$

(where $n = 1, 2, 3, \ldots$) and the reactants and inactive intermediate

$$H_2O_2 + C \overset{K_1}{\rightleftharpoons} CO + H_2O$$

Transformations absolutely similar to those given above make it possible to obtain the following expressions for the concentration of the intermediates:

$$[CO_{2n}] = \frac{K_{2n}[H_2O_2]^{2n}[C]_0}{1 + \sum\limits_n K_{2n}[H_2O_2]^{2n} + K_1[H_2O_2]} \tag{12.17}$$

where $[C]_0$ is the initial amount of the catalyst, and summation is conducted for all the active intermediates.

The total rate of decomposition of the peroxide is determined by the total effect of all the active forms:

$$-\frac{d[H_2O_2]}{dt} = \sum_n k_{2n}[CO_{2n}] \tag{12.18}$$

where $k_{2n}$ is the rate constant of intramolecular recombination of the active intermediate $CO_{2n}$.

From Eqs. (12.17) and (12.18) we obtain the following general expression for the rate of decomposition of hydrogen peroxide:

$$-\frac{d[H_2O_2]}{dt}=\frac{\sum_n k_{2n}K_{2n}[H_2O_2]^{2n}}{1+K_1[H_2O_2]+\sum_n K_{2n}[H_2O_2]^{2n}}[C]_0 \qquad (12.19)$$

For example, for the catalysis with molybdate ions considered above, Eq. (12.19) becomes

$$-\frac{d[H_2O_2]}{dt}=\frac{k_2K_2[H_2O_2]^2+k_4K_4[H_2O_2]^4}{1+K_1[H_2O_2]+K_2[H_2O_2]^2+K_4[H_2O_2]^4}[MoO_4^{2-}] \qquad (12.20)$$

It should be noted that it is practically good to conduct the process in such conditions when the concentrations of the separate intermediate forms may be neglected and to use not equations of the type (12.19) and (12.20), but considerably simpler limit forms of these equations. For example, catalysis with the ion $MoO_4^{2-}$ is frequently well described by the equation

$$-\frac{d[H_2O_2]}{dt}=\frac{k_2K_2[H_2O_2]^2}{1+K_1[H_2O_2]+K_2[H_2O_2]^2}[MoO_4^{2-}] \qquad (12.21)$$

and catalysis with the ion $Cr_2O_7^{2-}$ by the equation

$$-\frac{d[H_2O_2]}{dt}=\frac{k_2K_2[H_2O_2]^2}{1+K_2[H_2O_2]^2}[Cr_2O_7^{2-}] \qquad (12.22)$$

similar to Eq. (12.14) deduced on the basis of the assumption that an inactive intermediate form is absent.

Another interesting fact was discovered in the homogeneous catalytic decomposition of hydrogen peroxide. N. Petin and G. Bogdanov established that upon the joint action of two catalysts, the total effect sometimes greatly exceeds the sum of the actions of each of the catalysts separately. For example, in a weakly acid medium $CuSO_4$ does not accelerate the decomposition of $H_2O_2$, and $NaMoO_4$ accelerates it insignificantly. The joint use of these catalysts increases the rate of the reaction, which grows in proportion to the increase in the concentration of each of the catalysts. Several intermediates are formed in the reaction mixture. The molybdate forms compounds of the peroxide type, and the $CuSO_4$ forms at least two intermediates. In addition, common intermediates are formed. These are peroxides and consist of mixed molybdenum and copper compounds of the peroxide type. The kinetic analysis of such processes is quite complicated, and for this reason it will not be considered in this book.

**12.4. Acid-Base Catalysis.** There are quite many homogeneous catalytic reactions accelerated by hydroxyl and hydrogen ions in solutions. Reactions of this type include the esterification of acids and alcohols, the inversion of sugars, the halogenation of compounds containing the carbonyl group, and the saponification of esters.

The saponification of esters is catalyzed both by an acid and an alkali. In the latter case it proceeds according to a second-order reaction and can be described by the equation

$$CH_3COOC_2H_5+OH^- \longrightarrow CH_3COO^-+C_2H_5OH$$

Thus, here the hydroxyl ion is simultaneously one of the reactants and the catalyst. Table 12.4 gives the rate constants of reactions of saponification of ethyl acetate in solutions of hydroxides of selected metals. A glance at the table shows that the rate constant does not practically depend on the initial concentration of the ether and on the chemical nature of the alkali.

TABLE 12.4

**Rate Constants of Reactions of Saponification of Ethyl Acetate with Selected Alkalies**

| Alkali | Rate constant (in $dm^3/mol \cdot s$) at ether concentrations (in $dm^3/mol$) of | | |
|---|---|---|---|
| | 0.0500 | 0.0250 | 0.0125 |
| LiOH | 0.00639 | — | — |
| NaOH | 0.00636 | 0.00632 | 0.00621 |
| KOH | 0.00665 | 0.00646 | — |
| $Ca(OH)_2$ | — | 0.00606 | 0.00631 |
| $Sr(OH)_2$ | — | 0.00608 | — |
| $Ba(OH)_2$ | 0.00623 | 0.00629 | 0.00635 |
| Mean value | 0.00641 | 0.00624 | 0.00630 |

A change in the alkyl radical in esters of acetic acid also does not change the rate constant of the reaction, and very slightly changes the configuration conditions of an active collision (Table 12.5).

TABLE 12.5

**Parameters of Reactions of Saponification of Acetic Acid Esters**

$(CH_3COOR + OH^- \longrightarrow CH_3COO^- + ROH)$

| Ester | Rate constant, $dm^3/mol \cdot s$ | $P$ |
|---|---|---|
| $CH_3COOC_2H_5$ | $1.38 \times 10^7$ | $5 \times 10^{-2}$ |
| $CH_3COOC_3H_7$ | $1.94 \times 10^7$ | $7 \times 10^{-2}$ |
| $CH_3COOC_4H_9$ | $2.12 \times 10^7$ | $7 \times 10^{-2}$ |

It follows from these data that an ionic mechanism of the catalytic action is most probable, and that the main part in activation always belongs to the hydroxyl ions. Similarly when a reaction is accelerated by adding acids to the solution, the catalytic activity is mainly due to the hydrogen ions.

Already W. Ostwald noted that there is a single-valued relation between the catalytic activity of a system and its electrical conductivity for this and similar reactions. S. Arrhenius confirmed this

and, in addition, discovered that when a salt of the acid catalyzing a reaction is added to it, which according to the classical theory of electrolytic dissociation should reduce the concentration of the hydrogen ions, the catalytic effect not only does not decrease, but sometimes even grows (for example, in the esterification of trichloroacetic acid). This phenomenon was named the *secondary salt effect.* Since the addition of a salt to a solution of its acid increases the concentration of the anions and the undissociated acid, the existence of the salt effect indicates that both the undissociated acid and its anions have a catalytic activity.

Arrhenius also established that the addition of a neutral salt having no common ion with the acid catalyzing a reaction also sometimes leads to an increase in the catalytic action of the acid. For example, the rate of inversion of cane sugar in the presence of acetic acid grows by 30% when 10% (mole) of NaCl is added. This phenomenon is called the *primary salt effect.*

In some cases a reaction is accelerated catalytically only when an acid and a base are simultaneously present in the solution. This is observed, for example, for the reaction of mutarotation of glucose, studied in detail by T. Lowry (1925).

It was found that the alpha-form of glucose, which rotates the polarization plane through 109.6 degrees, rapidly loses its optical activity in an aqueous solution, reducing the angle of rotation to 52.3 degrees owing to the partial transition to the beta-form. The latter rotates the plane only through 32 degrees.

The mutarotation is accelerated when acids and bases are introduced into an aqueous solution of glucose. Depending on the concentration of the introduced compounds, the rate constant of the reaction can be found from the following empirical equation

$$k_{mut} = 0.0096 + 0.258\ [H_3O^+] + 9750\ [OH^-] \qquad (12.23)$$

Mutarotation completely stops in many organic solvents (for example, in pyridine, chloroform, *m*-cresol) in the complete absence of water, while in a mixture of one part of pyridine with two parts of *m*-cresol mutarotation proceeds twenty times faster than in water.

The cresol has only acid properties, and the pyridine only basic ones. Thus the simultaneous presence of both an acid (a donor of protons) and a base (an acceptor of protons) is essential for the catalytic mutarotation of glucose. Water can be both an acceptor and a donor of a proton:

$$\underset{\text{acid}}{H_2O} \rightleftharpoons H^+ + \underset{\text{base}}{OH^-}$$

$$H^+ + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+}$$

and therefore it itself can have catalytic action

As indicated above, the existence of the secondary salt effect forces us to acknowledge that acid anions and undissociated molecules also have catalytic activity. These facts were used in th' so-called *dualistic theory of catalysis* (H. Dawson, 1906). According to this theory, in calculating the rate of a catalytic process it must be taken into account that hydrogen and hydroxyl ions, anions, molecules of undissociated acids and bases and undissociated molecules of water are all catalytically active. Hence the rate of a reaction at the given concentration of a reactant is equal to the sum of the rates due to the activity of all the catalyzing particles.

According to this assumption, the total rate of a catalytic reaction will be equal to the sum of the rates due to the action of each of the catalysts:

$$J = k_{H^+}[H_3O^+] + k_{A^-}[A^-] + k_M[HA] + k_{OH^-}[OH^-] + k_w[H_2O] \quad (12.24)$$

where the symbols (subscripts) A, M and w denote respectively an anion, a molecule of an undissociated acid or base, and an undissociated molecule of water.

It can be seen from Eq. (12.24) that the rate of a reaction changes linearly with an increase in the concentration of the salt producing the anion $A^-$. At low concentrations of the salt, however, the minimum rate of the reaction is observed.

At great concentrations of the acid the action of $H_2O$ and $OH^-$ can be neglected, and Eq. (12.24) becomes

$$J = k_{H^+}[H_3O^+] + k_{A^-}[A^-] + k_M[HA] \quad (12.25)$$

Using the expression for the constant of dissociation of an acid

$$K = \frac{[H_3O^+][A^-]}{[HA]} \quad (12.26)$$

we find

$$[H_3O^+] = K\frac{[HA]}{[A^-]} \quad (12.27)$$

whence

$$J = Kk_{H^+}\frac{[HA]}{[A^-]} + k_{A^-}[A^-] + k_M[HA] \quad (12.28)$$

At high salt concentrations, the first and the last two terms of Eq. (12.24) may be neglected. Hence, on the basis of the equation

$$J = k_{A^-}[A^-] + k_M[HA] \quad (12.29)$$

we graphically find $k_{A^-}$ and $k_M$.

To take into consideration the action of water, let us introduce the notation

$$J_0 = k_{H^+}[H_3O^+] + k_{OH^-}[OH^-] + k_w[H_2O] \quad (12.30)$$

Hence

$$J = J_0 + k_{A^-}[A^-] + k_M[HA] \quad (12.31)$$

If, while measuring the rate, we consecutively dilute the system with water, the ratio

$$\frac{[HA]}{[A^-]} = q \quad (12.32)$$

will be constant, and inserting Eq. (12.32) into Eq. (12.31), we get

$$J = J_0 + k_{A^-}[A^-] + k_M[A^-]q = J_0 + (k_{A^-} + k_M q)[A^-] \quad (12.33)$$

Graphical solution of this equation gives the values of $J_0$ and $k_{A^-} + k_M q$ (Fig. 12.2).

Taking into account the product of the solubility of water

$$K_w = [H_3O^+][OH^-] \quad \text{or} \quad [OH^-] = \frac{K_w}{[H_3O^+]} \tag{12.34}$$

we get

$$J_0 = k_{H^+}[H_3O^+] + \frac{K_w k_{OH^-}}{[H_3O^+]} + k_w[H_2O] \tag{12.35}$$

Differentiation of this expression and equating of the derivative to zero yield

$$\frac{\partial J_0}{\partial [H_3O^+]} = k_{H^+} - \frac{K_w k_{OH^-}}{[H_3O^+]^2} = 0 \tag{12.36}$$

whence

$$[H_3O^+] = \sqrt{\frac{K_w k_{OH^-}}{k_{H^+}}}$$

and

$$k_{OH^-} = \frac{k_{H^+}[H_3O^+]^2}{K_w} \tag{12.37}$$

Inserting the value of $k_{OH^-}$ from Eq. (12.37) into Eq. (12.35), we obtain the experimentally found minimum rate:

$$J_{0,\min} = k_{H^+}[H_3O^+]_{\min} + k_{H^+}[H_3O^+]_{\min} + k_w[H_2O] \tag{12.38}$$

whence comparing Eq. (12.38) with the initial equation (12.30) for $J_0$, we get

$$k_{H^+}[H_3O^+]_{\min} = k_{OH^-}[OH^-]_{\min} \tag{12.39}$$

i.e. the catalytic action of the ions $H_3O^+$ and $OH^-$ at the minimum point is the same. This point is called an *isocatalytic* one.

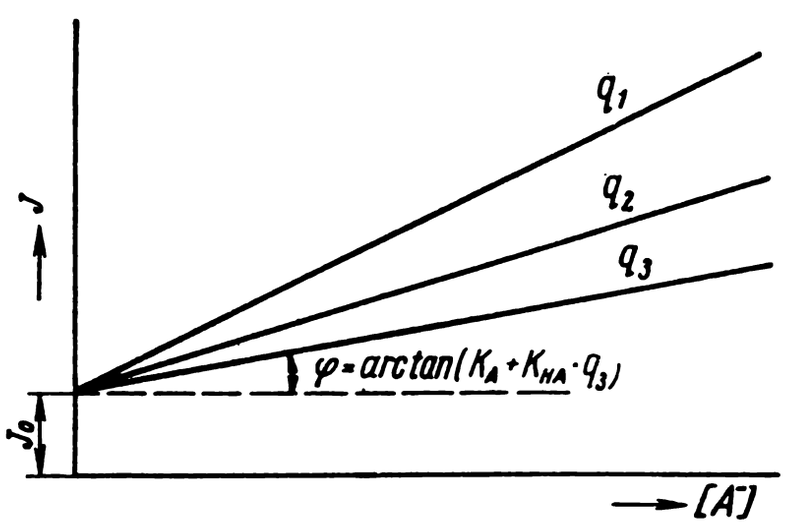



Fig. 12.2. Graphical solution of Eq. (12.33)

Thus, by changing the conditions of an experiment, we can, according to the dualistic theory of catalysis, use the experimental data to determine the numerical values of the kinetic constants in the rate equation.

As to the primary salt effect, it can only be explained on the basis of the Debye-Hückel theory of strong electrolytes (see Sec. 16.5). The introduction of a salt not containing common ions with the components of the mixture changes

the ionic strength (see Sec. 18.17) of the solution, as a result of which the degrees of dissociation of the substances and the concentration of the particles catalyzing the reaction change.

**12.5. Influence of Ionic Strength on Rate of Reaction.** The concentrations of the reactants figure in all equations of chemical kinetics. In thermodynamics the equilibrium constant of a non-ideal system is expressed through the activities. This circumstance must be taken into account if a kinetic equation contains the equilibrium constant. True, in reactions in a gaseous phase and between neutral molecules in a solution it can be neglected, but for reactions between charged particles, the failure to take this into consideration may be the source of appreciable errors.

For the rate constant of the bimolecular reaction

$$A + B \rightarrow AB^{*} \rightarrow \text{Products}$$

proceeding in a solution, the activated complex theory gives

$$k_r = \chi \frac{kT}{h} \frac{c_{AB^*}}{c_A c_B} \tag{12.40}$$

Here $k$ is the Boltzmann constant, and the symbol $k_r$ is used for the rate constant.

The thermodynamic constant of equilibrium between the reactants and the activated complex is

$$K^{*} = \frac{a_{AB^*}}{a_A a_B} = \frac{c_{AB^*}}{c_A c_B} \frac{\gamma_{AB^*}}{\gamma_A \gamma_B} \tag{12.41}$$

Combining Eqs. (12.40) and (12.41), we get the Brönsted-Bjerrum equation

$$k_r = \chi \frac{kT}{h} K^{*} \frac{\gamma_A \gamma_B}{\gamma_{AB^*}} = k_0 \frac{\gamma_A \gamma_B}{\gamma_{AB^*}} \tag{12.42}$$

for the rate constant of a reaction proceeding in any non-ideal medium. The quantity $k_0$ is the rate constant for an infinitely dilute solution, i.e. at $\gamma = 1$.

To use Eq. (12.42) in a specific case, an analytic expression for the activity coefficients must be selected. If we select infinite dilution as the standard state, the theory of electrolytes gives the following approximate relation for the activity coefficient:

$$\gamma = e^{-Az^2 \sqrt{I}} e^{\beta I} \tag{12.43}$$

where $A$ = constant, which for aqueous solutions at 25 °C is approximately equal to 0.51
$z$ = charge number of ion
$I$ = ionic strength of solution
$\beta$ = constant approximately inversely proportional to the radius of an ion.

If $z_A$ and $z_B$ are the respective charges (charge numbers) of the reacting particles, the reaction can be written in the form

$$A^{z_A} + B^{z_B} \rightarrow AB^{*(z_A+z_B)} \rightarrow \text{Products}$$

and insertion of the corresponding values of the activity coefficients in the Brönsted-Bjerrum equation gives

$$k_r = k_0 e^{-0.51[z_A^2+z_B^2-(z_A+z_B)^2]\sqrt{I}} e^{(\beta_A+\beta_B-\beta_{AB^*})I} =$$

$$= k_0 e^{1.02 z_A z_B \sqrt{I}} e^{(\beta_A+\beta_B-\beta_{AB^*})I} \qquad (12.44)$$

or

$$\ln k_r = \ln k_0 + 1.02 z_A z_B \sqrt{I} + (\beta_A + \beta_B - \beta_{AB^*}) I \qquad (12.45)$$

Let us consider two cases.

1. *Interaction between Charged Particles.* The sum $(\beta_A + \beta_B - {}_{AB^*})$ is small, and for interaction between two ions the second addend in Eq. (12.45) may be neglected, i.e.

$$\ln k_r \approx \ln k_0 + 1.02 z_A z_B \sqrt{I} \qquad (12.46)$$

Consequently, the logarithm of the rate constant, according to the theory, should be a linear function of the square root of the ionic strength, while the tangent of the angle of inclination of the straight line is determined by the ratio of the charges of the reacting particles. Figure 12.3 gives experimental data for six reactions with different values of the product $z_A z_B$ in the coordinates $\log k_r/k_0$ versus $\sqrt{I}$. A glance at the figure shows that theory and experimental data coincide quite satisfactorily, discrepancies being observed only at high concentrations.

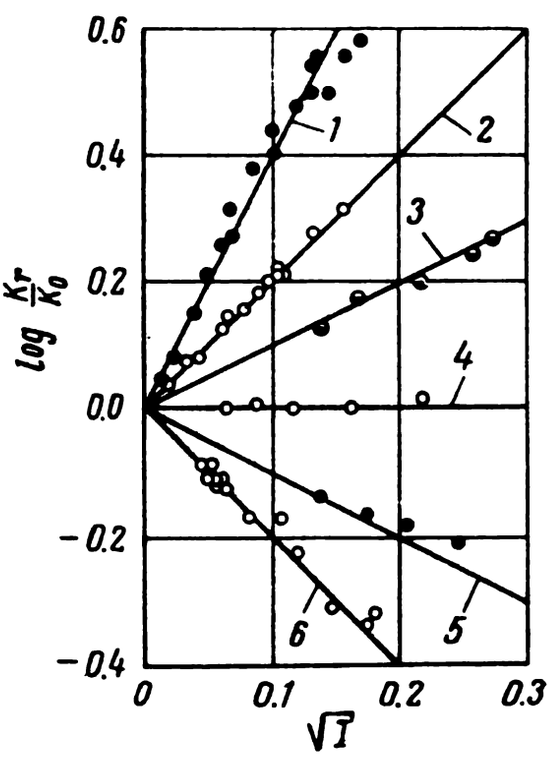



Fig. 12.3. Logarithm of rate constant versus square root of ionic strength for reactions between ions:

1 — $[Co(NH_3)_5Br]^{2+} + Hg^{2+}$; 2 — $S_2O_8^{2-} + I^-$; 3 — $ON{=}N{-}COO{-}C_2H_5^- + OH^-$; 4 — $CH_3COOC_2H_5 + OH^-$; 5 — $H_2O_2 + H^+ + Br^-$; 6 — $[Co(NH_3)_5Br]^{2+} + OH^-$

2. *Interaction between an Ion and a Neutral Molecule.* According to Eq. (12.43), the activity coefficient for a neutral molecule is

$$\gamma = e^{\beta I} \qquad (12.47)$$

and for the reaction

$$A + B^{z_B} \rightarrow AB^{*z_B} \rightarrow \text{Products}$$

from Eq. (12.44) we get

$$k_r = k_0 e^{(\beta_A + \beta_B - \beta_{AB^*})I} \tag{12.48}$$

The low value of the sum $(\beta_A + \beta_B - \beta_{AB^*})$ makes it possible to expand the exponent into a series, neglecting the terms of the higher powers for not very great values of $I$:

$$k_r \approx k_0 [1 + (\beta_A + \beta_B - \beta_{AB^*}) I] \tag{12.49}$$

Consequently, in the case considered above the rate constant should be directly proportional to the ionic strength. Figure 12.4 gives, in the coordinates $k_r/k_0$ versus $I$, experimental data for the hydrolysis of ethylene acetal catalyzed by a 0.1 $N$ solution of $HClO_4$ with different amounts of additions NaCl, $KNO_3$, $NaNO_3$ and $NaSO_3C_2H_5$ (here $k_0$ is the rate constant in the absence of additions). The clear linear relation shows that Eq. (12.49) well agrees with experimental data.

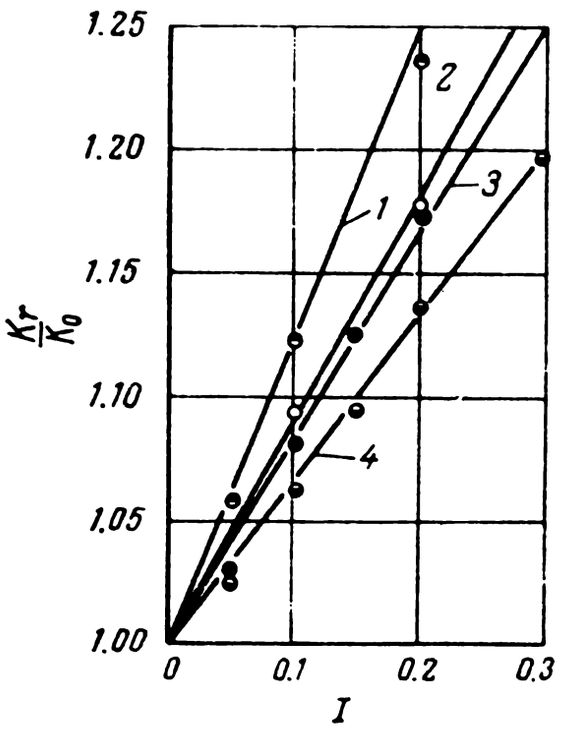



Fig. 12.4. Relative increase in rate constant for hydrolysis of ethylene acetal depending on ionic strength of solution; the reaction is catalyzed by a 0.1 $N$ solution of $HClO_4$ in the presence of:
1—NaCl; 2—$KNO_3$; 3—$NaNO_3$; 4—$NaSO_3C_2H_5$

## *Heterogeneous Catalytic Reactions*

**12.6. Development of Theory of Heterogeneous Catalysis.** The first heterogeneous catalytic reaction to be observed was the dehydration of ethyl alcohol on activated clay carried out by J. Priestley (1778):

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

Metal catalysts were first used by M. van Marum (1796), who dehydrated ethyl alcohol

$$C_2H_5OH \longrightarrow C_2H_4O + H_2$$

on copper, iron, nickel, silver and cerium. In the first half of the 19th century many investigations were devoted to heterogeneous catalysis. Oxidizing reactions in the gaseous phase on metals (H. Davy), the decomposition of ammonia and hydrogen peroxide (L. Thénard), the hydration of ethylene on platinum (M. Faraday), and the oxidation of ammonia on platinum (C. Kuhlmann) were among the many catalytic processes discovered.

Much research was devoted to a theoretical explanation of the catalytic action of a solid. The first ideas on the relation of catalytic phenomena to adsorption are connected with Faraday's name.

J. Berzelius, who occupied idealistic positions, attempted to explain a catalytic process with the aid of the idea of the so-called catalytic force that he introduced. J. Liebig considered that the causes of catalytic transformations were the mechanical action of a solid on the molecules of the reactants.

The further development of the theory of catalysis followed both the experimental path of accumulating data, developing ways of preparing active catalysts, discovering and studying new catalytic processes, introducing catalysis into the chemical industry, and a theoretical path. The achievements of the theoreticians, however, were considerably more modest than those of experimentators. And this is not by chance. There is no difference of principle between catalytic and non-catalytic processes, both obey the main laws of chemical kinetics, both systems of reactants pass through a special activated state having an increased energy, nevertheless heterogeneous catalytic reactions have their own special features. First of all there is a solid on whose properties and state all the phenomena as a whole appreciably depend. This is why it is not accidental that the achievements of the theory of heterogeneous catalysis are intimately related to the development of the theory of solids. Since a process proceeds on the surface, a knowledge of the structure of the surface of a catalyst is decisive for development of the theory of catalysis. Hence follows the close relation between the development of the theory of catalysis and the development of experimental and theoretical investigation of adsorption phenomena. The complicated nature of heterogeneous processes and their specific features lead to the fact that the theoretical investigations in this field have not yet been completed by the construction of theoretical conceptions that could serve as the basis for generalization of the available data. Meanwhile we can only speak of the existence of several theories which in the first approximation generalize certain experimental data.

**12.7. Steps of Heterogeneous Catalytic Processes.** Two types of heterogeneous catalysis are most frequently encountered in practice, namely, processes in which the catalyst is in the solid phase and the reactants in the liquid one, and processes in which the catalyst is in the solid phase and the reactants in the gaseous one. The reaction, as a rule, proceeds (in certain multistep processes it begins) on the phase interface, i.e. on the surface of the solid—the catalyst. A heterogeneous process can be divided into five steps: (1) transportation of the reactants to the surface of the catalyst (diffusion); (2) adsorption of the reactants on the surface of the catalyst; (3) reaction on the surface of the catalyst; (4) desorption of the products with freeing of the surface of the catalyst; and (5) transportation of the products into the bulk.

Depending on the conditions in which a process is conducted and

its features, any of the five steps may be the slowest one. Hence, the rate of the catalytic process may be limited by one of them. The determining factor for comparing the activity of catalysts is the rate of the reaction on the surface. For this reason when it is important to determine the activity of a catalyst, every effort is made to so conduct a process that its rate will be determined by the third so-called kinetic step.

Of special importance for heterogeneous processes is the transfer of a substance from the bulk of a liquid or gas to the solid surface.

Below we shall consider in detail in what cases the rate of a process is determined by the diffusion of the reactants toward the active parts or centres of a system. Now we shall briefly characterize the kinetic aspect of diffusion.

Fick's law for diffusion in a given direction is

$$dn = -DA\frac{dx}{dl}dt \tag{12.50}$$

where $dn$ = amount of substance passing during the time $dt$ through a surface with the area $A$

$D$ = diffusion coefficient

$\frac{dx}{dl}$ = gradient of concentration.

Assume that at the phase interface the concentration of a reactant is equal to $c_s$, and at a certain distance $\delta$ from it to $c_x$. Hence

$$-\frac{dx}{dl} = \frac{c_s - c_x}{\delta} \tag{12.51}$$

and

$$dn = DA\frac{c_s - c_x}{\delta}dt \tag{12.52}$$

Dividing the right-hand and left-hand parts of Eq. (12.52) by the volume and passing over to concentrations, we get

$$\frac{dn}{V} = dc = \frac{DA}{V}\frac{c_s - c_x}{\delta}dt \tag{12.53}$$

We finally obtain for the rate of the diffusion process

$$\frac{dc}{dt} = \frac{DA}{V\delta}(c_s - c_x) \tag{12.54}$$

Thus the rate of diffusion kinetically obeys a first-order equation relative to the concentration in the bulk of the solution ($c_x$), which is confirmed by experimental data.

The rate of diffusion grows with the temperature according to a law similar to the Arrhenius equation

$$D = ke^{-E/RT} \tag{12.55}$$

It should be noted, however, that the value of $E$ rarely exceeds 1000-2000 cal/mol, i.e. it is only a small fraction of the activation

energies of most chemical reactions. Consequently, with a growth in temperature, the rate of diffusion will increase considerably slower than the rate of a chemical process.

**12.8. Features of Heterogeneous Catalytic Processes.** Let us discuss the main features discovered in studying heterogeneous catalytic phenomena.

1. *Affinity of Reactants to Catalyst.* The empirical rule that a catalyst has chemical affinity to one or several of the reactants is constantly confirmed in practice. For example, the hydrogenation and dehydrogenation catalysts Pt, Ni and Cu easily form surface compounds of the chemisorption type Pt—H, Ni—H and Cu—H with hydrogen. Palladium is even capable of dissolving hydrogen, the result being destruction of the crystal lattice of the metal, i.e. interaction between the hydrogen and palladium passes from the surface into the bulk. Hydrating and dehydrating catalysts, for example $Al_2O_3$ or $Al_2(SO_4)_3$, are capable of forming compounds of the hydrate type with water. Their action in the dehydration of alcohols is similar to that of sulphuric acid (a typical dehydrating substance). The same can be said of oxidizing catalysts. Platinum and palladium form sorption surface compounds of the type $Pt\begin{matrix}O\\|\\O\end{matrix}$ and $Pd\begin{matrix}O\\|\\O\end{matrix}$ with oxygen. Copper oxide CuO is easily reduced to metal copper and again oxidized to CuO. Vanadium and osmium form oxides with a different oxygen content that easily transform into one another. Thus, the affinity of a catalyst to reactants ensures the formation of an intermediate which frequently has an unstable nature and readily decomposes into the products with regeneration of the catalyst.

The problem of the interaction between a catalyst and the reactants was considered theoretically by D. Mendeleev, who was the first to indicate that "an intermediate form of reaction can be detected in catalytic phenomena". In classifying chemical processes, Mendeleev considers three classes of transformations: (1) the absorption of one substance by another (in modern terminology—sorption); (2) mutual transformation of two substances—a non-catalytic chemical reaction; (3) the transformation of one substance as a result of the action on it of another substance that remains unchanged at the end of the process—catalysis. According to Mendeleev, the essence of a heterogeneous (contact) process consists in the following. Firstly, in the contact without fail of the reactants with the catalyst, as a result of which "there may occur a reaction either of decomposition, or combination, or substitution, or two kinds of these reactions simultaneously"; secondly, in that upon contact the nature of the intra-atomic motions in the reacting molecules changes resulting in their transition to a state that is reactive in a definite direction. Thus Mendeleev's theory contains assumptions that later formed the foundation of two theoretical conceptions which developed separately for a long time. These are the *chemical theory* and the *physical theory*. The former is called the *theory of intermediates*, and its development is connected with the names of P. Sabatier and J. Senderens. According to this theory

the determining part in catalytic reactions is played by an unstable intermediate. The physical theory represents different variants of the adsorption theory and the so-called *theory of deformation* according to which adsorption is accompanied by weakening (in the limit—breaking) of the bonds in the molecules which then leads to their redistribution. These views were confirmed in the work of N. Zelinsky's school in the field of organic catalysis, on the basis of which the specific models of the multiplet theory were developed in the long run.

2. *Selective Action of a Catalyst.* An important property of a catalyst is the selective nature of its action. This implies the following. For the same reactants different catalysts are capable of causing different processes with the formation of different products. Thus, a mixture of carbon monoxide and hydrogen (water gas) can produce different products, depending on the catalyst and the conditions in which the experiment is conducted. If the reaction is conducted over metal nickel at 240-260 °C, methane is formed:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

On copper at an increased pressure methyl alcohol is synthesized:

$$CO + 2H_2 \longrightarrow CH_3OH$$

On metal cobalt a mixture of higher olefins and paraffins is formed, on metal ruthenium at an increased pressure solid paraffins with a molecular mass of the order of several thousands are formed.

The number of products that can be obtained in the catalytic transformations of ethyl alcohol is not smaller. On aluminium oxide at 350 °C dehydration of the alcohol occurs with the formation of ethylene:

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

On the same aluminium oxide at 250 °C dehydration in the main leads to the synthesis of an ether:

$$2C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2O$$

On active copper at 200 °C dehydration proceeds with the formation of aldehyde:

$$C_2H_5OH \longrightarrow CH_3CHO + H_2$$

and on specially prepared copper catalysts ethyl acetate

$$2C_2H_5OH \longrightarrow CH_3COOC_2H_5 + 2H_2$$

and acetone

$$2C_2H_5OH \longrightarrow CH_3COCH_3 + 3H_2 + CO$$

may form.

Butadiene is synthesized on zinc chromate catalysts:

$$2C_2H_5OH \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2 + 2H_2O$$

As a result of the catalytic action of metal sodium butyl alcohol is formed:

$$2C_2H_5OH \longrightarrow C_4H_9OH + H_2O$$

The reasons for the selective action of the catalysts in each particular case may be different. In the early stage of the development of the theory of catalysis, the most general explanation was the one given on the basis of the properties of the intermediates. At present these assumptions are frequently detailed on the basis of the adsorption properties of a catalyst and its structure.

3. *Mixed Catalysts.* Catalysts are frequently used not in the form of pure substances, but in the form of complicated multicomponent systems. The object is to impart a greater selectivity to the catalyst, increase its thermal resistance and mechanical strength, and also to increase its activity. Of the greatest interest are three types of such catalysts, namely, *mixed*, *supported* and *promoted* catalysts. These terms are somewhat conditional and correspond rather to the physical state of the prepared catalyst than to the method of its preparation.

Mixed catalysts, as a rule, are a mixture of two or more oxides, for example $Al_2O_3 + ThO_2$, $Al_2O_3 + Cr_2O_3$, $CoO + MgO$. The composition of these catalysts can be changed, and their activity is frequently a function of composition. There is sometimes less oxygen in a mixed catalyst than there should be according to the stoichiometric equation. Such catalysts are, as it were, a transition to metal alloys used as catalysts.

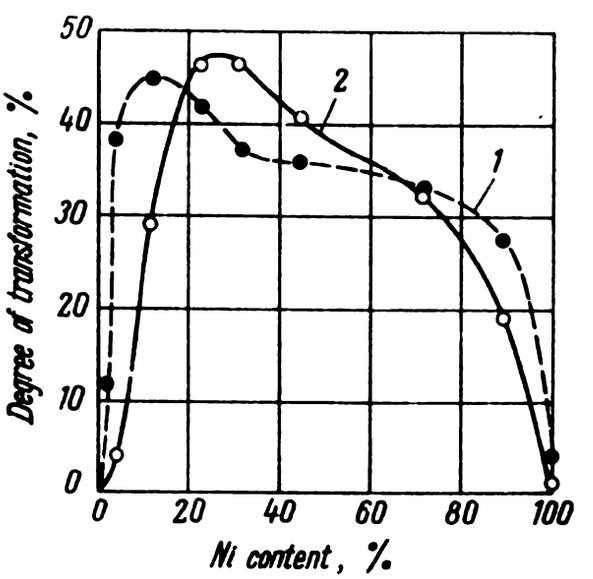



Fig. 12.5. Dependence of degree of transformation on Ni content in catalyst for reactions of:
1—reduction of acetone; 2—hydration of benzene

Mixed catalysts are most frequently prepared by joint precipitation from their salts. For example, to prepare a mixed nickel and magnesium oxide catalyst, precipitation is conducted from a solution of magnesium and nickel nitrates of the appropriate concentration (depending on the desired composition). Precipitation can be performed, for example, with oxalate ions. The oxalates formed are reduced in a stream of hydrogen or are decomposed in a vacuum with heating to 450-500 °C. The result is a catalyst $Ni + MgO$, in which the amount of oxygen stoichiometrically corresponds to that of the magnesium. Figure 12.5 shows how the activity of the mixed catalyst ($Ni + MgO$) depends on the Ni content for two processes, namely, the hydration of benzene

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$$

and the reduction of acetone

$$CH_3COCH_3 + H_2 \rightarrow CH_3CH(OH)CH_3$$

The maximum activity of the catalyst in the hydration of benzene is observed for a nickel content of 22%, and in the reduction of acetone of 11%. This indicates the selectivity with respect to the composition of the catalyst and that the two processes considered above apparently proceed with different activated centres.

4. *Catalyst Poisoning*. The presence in a reaction system of certain substances, frequently in a negligible amount, is capable of decreasing or completely suppressing the activity of a catalyst. Such substances have been called *catalyst poisons*, and the phenomenon itself—*catalyst poisoning*. Typical poisons of some hydration catalysts (Ni, Pt) are compounds of sulphur ($H_2S$, $CS_2$, thiophene, mercaptans, etc.), hydrocyanic acid and some of its derivatives, carbon monoxide, free halogens, mercury and some of its salts, compounds of phosphorus, arsenic, lead, etc. In the majority of cases a catalyst is poisoned as a result of adsorption of the poison on its surface. Thus, the mechanism of poisoning consists in blocking the active centres of the catalyst. Since adsorption may be either reversible or irreversible, there is respectively distinguished *reversible* and *irreversible* poisoning. Thus, a platinum catalyst is poisoned by CO and $CS_2$, but when it is introduced in a pure mixture of the reactants (gaseous), desorption of the poison occurs and the activity is restored. When poisoned with $H_2S$ and $PH_3$, however, platinum becomes completely deactivated. Figure 12.6 shows the kinetics of the reversible poisoning of an iron catalyst by water vapour in the synthesis of ammonia. When a moist gas is passed through the reactor, the catalyst activity drops to about one-sixth of the initial value, while when a dry mixture of nitrogen and hydrogen is passed through, the activity is restored to its initial value during an hour.

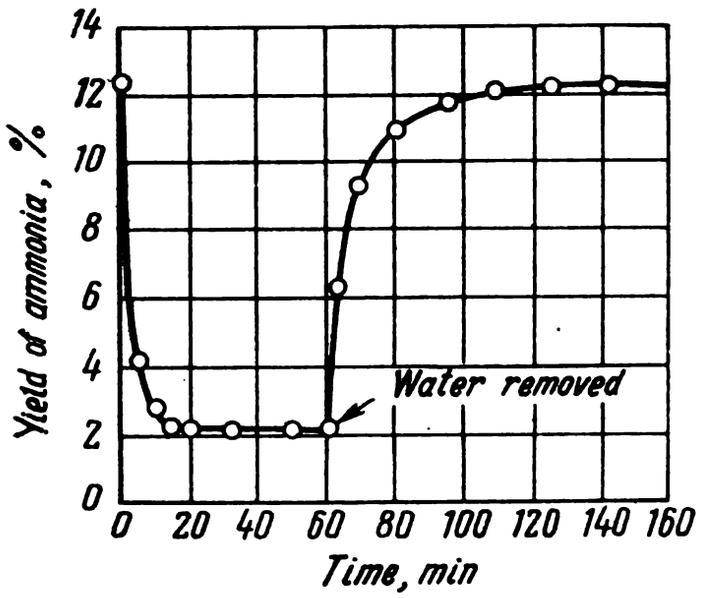



Fig. 12.6. Reversible poisoning of iron catalyst by water in the synthesis of ammonia

It should be underlined that already quite small amounts of a poison appreciably, and sometimes completely, deactivate a catalyst. Figure 12.7 shows typical poisoning isotherms for platinum black (the dependence of the catalyst activity on the amount of poison at constant temperature). The first portions of the poison sharply reduce the catalyst activity (by 70-80%), then the toxicity of the poison decreases. As a whole the poisoning isotherms most

frequently obey the exponential law

$$\frac{A_p}{A_0} = e^{-\alpha c} \qquad (12.56)$$

where $A_p$ = activity of poisoned catalyst
$A_0$ = activity of pure catalyst
$c$ = amount of poison adsorbed by catalyst
$\alpha$ = poisoning coefficient depending on the nature and properties of the catalyst and certain parameters of the process.

When the amount of poison is small, however, the following linear approximation is true:

$$\frac{A_p}{A_0} = 1 - \alpha c \qquad (12.57)$$

i.e. at first the mechanism of simple blocking of the active centres by poison molecules holds. At great amounts of the poison its useless loss begins to tell (from the viewpoint of the toxic effect) as a result of adsorption on inactive portions of the surface.

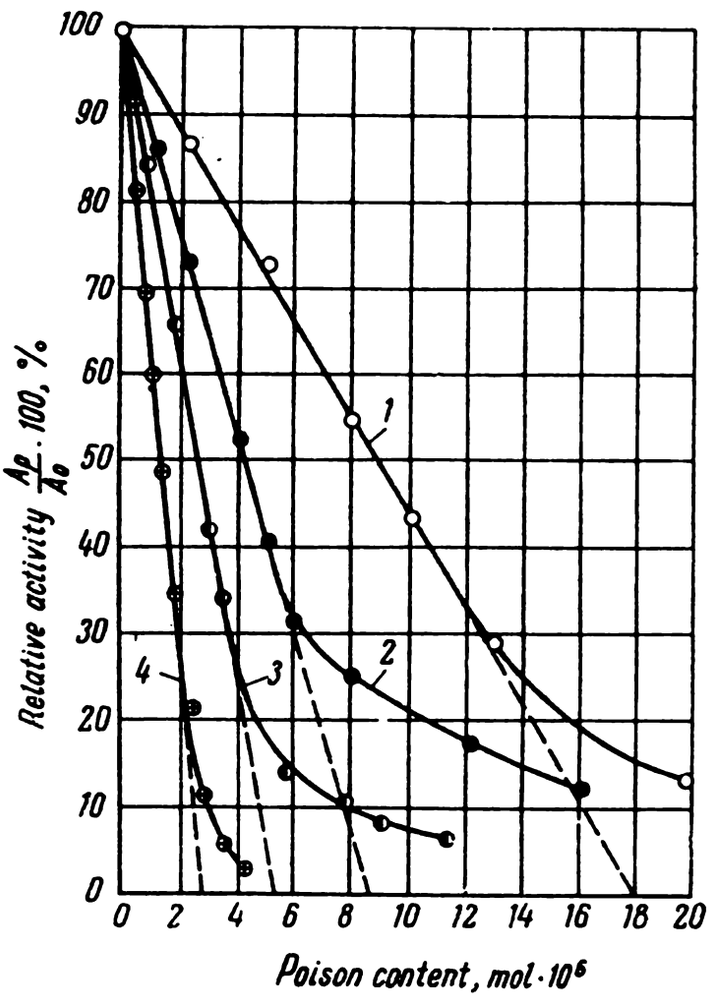



Fig. 12.7. Dependence of activity of platinum catalyst on poison content:
1—hydration of cyclohexane (poison—pyridine); 2—hydration of crotonic acid (poison—cyanions); 3—ditto (poison—hydrogen arsenide); 4—ditto (poison—thiophene)

Investigations of the process of poisoning played a great role in the development of the theory of catalysis. The following practical conclusion can be made from the results of these investigations. It is necessary to carefully protect catalysts from poisoning and make special demands to the apparatus and the purification of the reactants.

5. *Promoted Catalysts.* The activity of a catalyst is frequently increased when during its preparation a substance is added to it which by itself has no catalytic properties for the given process. Such substances have been called *promoters*, and the phenomenon itself *promotion.* Two kinds of promoting action are distinguished, namely, *structural promotion* and *modification.*

Structural promoters stabilize the active phase of the catalyst, for example with respect to heating or other actions. Their role

apparently consists in increasing the service life of the microcrystalline phase of the catalyst, which is not stable owing to thermodynamically spontaneous thermal recrystallization (consolidation) of the minute catalyst crystals. A well studied example of such action of a promoter is the promoting by aluminium oxide of the iron catalyst in ammonia synthesis. The activity of the catalyst prepared by reducing $Fe_3O_4$ at 550 °C and 100 atm rapidly diminishes during the process. The addition of a small amount of $Al_2O_3$ doubles the initial activity of the catalyst and maintains its stability during a considerable period of time. The addition of the promoter also results in an increase in the specific surface of the catalyst. Thus, iron reduced from pure $Fe_3O_4$ has a surface area of $A = 0.55$ m²/g, while iron reduced from $Fe_3O_4$ promoted with 1% of $Al_2O_3$ has an area of $A = 9.44$ m²/g. The increase in the specific area explains the increase in activity, but the stability of the catalyst is due to other reasons. Aluminium oxide forms with $Fe_3O_4$ a crystal lattice of spinel $Al_2O_4Fe$, isomorphous with $Fe_2O_4Fe$, and for this reason part of the $Fe^{3+}$ ions are replaced by $Al^{3+}$ ones. A comparative investigation of the adsorption of nitrogen and carbon monoxide, which are specifically chemisorbed on aluminium ions, has shown that this mixed structure is mainly formed on the surface of the catalyst. Thus aluminium oxide forms a reticular film on the surface of the minute iron crystals that prevents the processes of recrystallization.

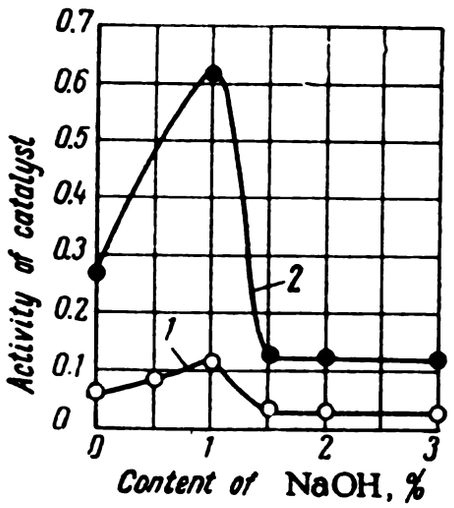



Fig. 12.8. Modification of catalyst $WO_3$ with sodium hydroxide in deep oxidation of isooctane:
1—at 320 °C; 2—at 420 °C

The modification of catalysts discovered by S. Roginsky (1940) consists in that the same additions, depending on their concentration, may have either a poisoning or a promoting action. Modifying promoters change the structure and chemical composition of the active phase. It is possible that their role consists in the synthesis of active centres of a new chemical nature on the surface of the catalyst, and in this connection a change in the selectivity is sometimes also observed in modification. Figure 12.8 shows a typical example of modifying action. The activity of the catalyst $WO_3$ in the deep oxidation of isooctane is given depending on additions of NaOH. The maximum activating action of the NaOH is reached when 1% of it is added; further addition of the modifier (over 1.5% of NaOH) already leads to a reduction in the activity of the catalyst to below its initial value. The addition of $K_2O$ to the iron catalyst in the synthesis of ammonia also has a modifying nature. The addition

of $K_2O$ to the iron catalyst not promoted with aluminium oxide reduces its catalytic activity. Conversely, the addition of $K_2O$ to promoted iron results in a clear activating effect. Lately serious attention has been attracted by attempts to explain promoting action on the basis of electron notions (F. Wolkenstein).

6. *Activation in Heterogeneous Catalytic Reactions.* In the majority of cases the Arrhenius equation is true for the rate constant of a heterogeneous catalytic reaction:

$$k = Ce^{-E/RT} \tag{12.58}$$

The physical meaning of the constants $C$ and $E$, however, requires clarification in this case. Omitting cases when the introduction of a heterogeneous catalyst into a system changes the direction of the processes, let us compare the rates of a non-catalytic and a catalytic reactions when the direction of the process does not change and the functions of the catalyst consist only in acceleration of the process. It is obviously necessary here to take both constants of the Arrhenius equation ($C$ and $E$) into account, since the ratio of the rate constants of a catalytic and non-catalytic reactions is equal to

$$\frac{k_{cat}}{k} = \frac{C_{cat}}{C} e^{(E-E_{cat})/RT} = \frac{C_{cat}}{C} e^{\Delta E/RT} \tag{12.59}$$

Here the subscripts have been omitted for the non-catalytic reaction, while $k_{cat}$ is the rate constant, $C_{cat}$ is the preexponential factor and $E_{cat}$ is the activation energy determined from experiments according to the relation $\log k_{cat} = f\,(1/T)$ of the catalytic reaction. The quantity $E_{cat}$ is called the *apparent activation energy*[1].

Let us first consider the part played by the exponential factor in changing the rate, i.e. the physical meaning of the quantity $\Delta E$, which is the difference between the activation energies of the non-catalytic and catalytic reactions.

Let the following bimolecular reaction proceed in the absence of the catalyst:

$$A + B \longrightarrow AB^{*} \longrightarrow \text{Products}$$

and let its rate grow in the presence of catalyst C, without the products changing. Assume that the active adsorption state is similar to the non-catalytic activated complex $AB^{*}$, but owing to adsorption on the catalyst weakening of the bonds occurs, which facilitates their redistribution and the formation of the products with a lower total consumption of energy. The entire process can now be depicted as follows.

[1] This term is based on the consideration that $E_{cat}$ is not the energy necessary for transition of the adsorbed state of the reactants into an activated one. On the other hand, it is this energy that is actually necessary for transferring the unadsorbed reactants into an activated state, adsorbed on the catalyst. It is the latter circumstance that makes the term *apparent activation energy* unsuccessful.

1. Adsorption of the reactants on the surface of the catalyst:

$$A + B + C \longrightarrow ABC$$

This process, as a rule, is an activated and exothermic one, i.e. state ABC will have a lower potential energy in comparison with state A + B + C.

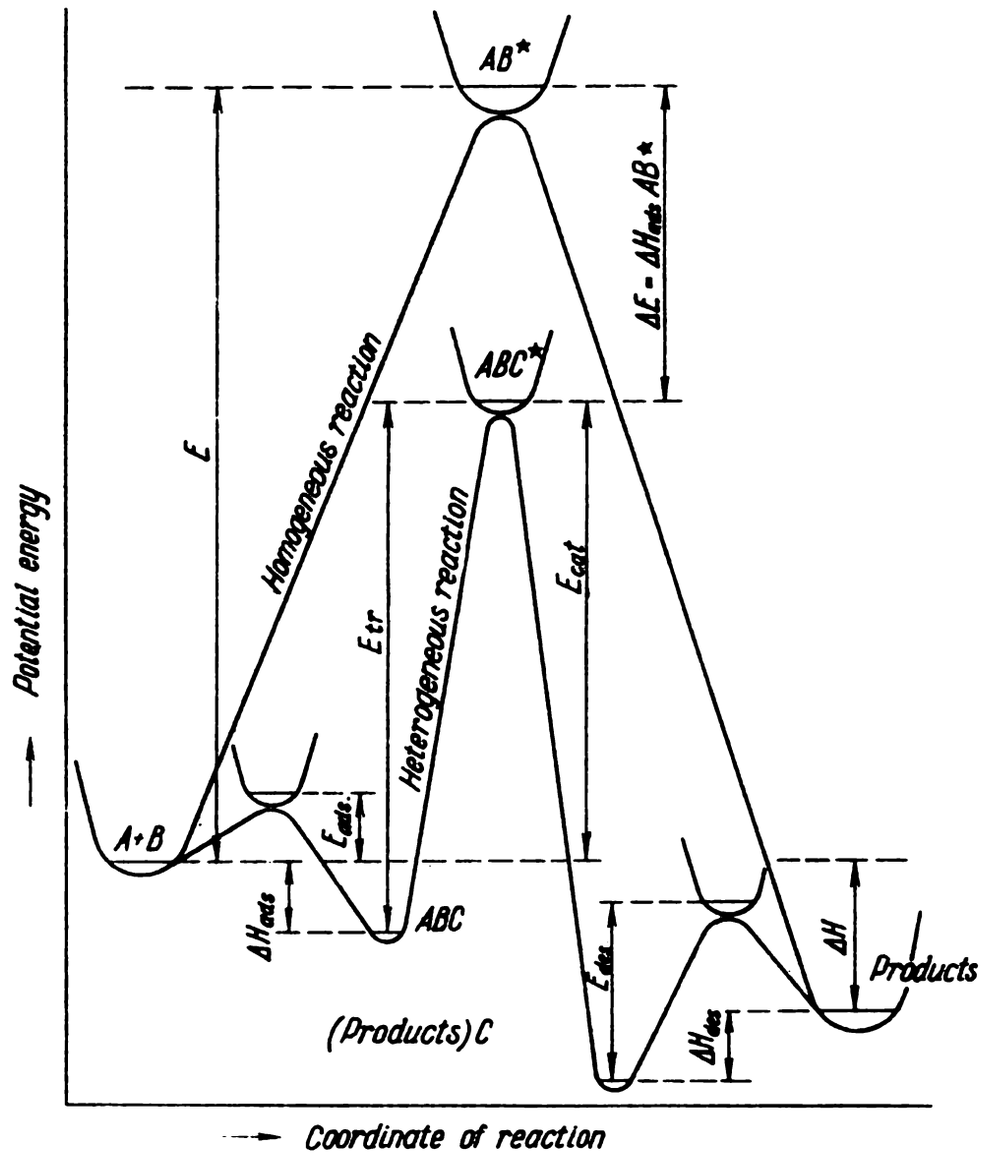



Fig. 12.9. Curve of potential energy along reaction coordinate for a heterogeneous catalytic process

2. Transfer of the adsorbed state into an active one:

$$ABC \longrightarrow ABC^*$$

This process requires the expenditure of a certain energy $E_{tr}$, called the *true energy of activation* of a heterogeneous catalytic reaction.

3. Reaction in the adsorbed state with the formation of the adsorbed products:

$$ABC^* \longrightarrow (\text{products})\,C$$

4. Desorption of the products leading to regeneration of the catalyst:

$$(\text{products})\ C \longrightarrow C + \text{Products}$$

This process is also activated, as a rule, but endothermic.

The sequence considered above is depicted graphically in Fig. 12.9. A glance at this figure shows that the quantity $\Delta E$ is the enthalpy of adsorption of the activated complex on the catalyst. Such an interpretation is naturally true only with account of the assumption made on the similarity of the activated complexes in the non-catalytic and catalytic reactions. In the general case this quantity may also include the change in the enthalpy due to energy and configurational transformations within the activated complex. Here a different factor is of significance, namely, the adsorption process is exothermic ($\Delta E > 0$), as a result of which the catalytic process is accelerated in comparison with the non-catalytic one[1]. Experiments entirely confirm this conclusion. Table 12.6 gives comparative data on the activation energies of selected homogeneous (non-catalytic) and heterogeneous (catalytic) reactions.

TABLE 12.6

**Activation Energies of Homogeneous and Heterogeneous Reactions**

| Reaction | $E$, cal/mol | Catalyst | $E_{cat}$, cal/mol | $\Delta E$, cal/mol | $e^{\Delta E/RT}$ at 600 K |
|---|---|---|---|---|---|
| $2HI \longrightarrow H_2 + I_2$ | 44 000 | Pt | 14 000 | 30 000 | $8.8 \times 10^{10}$ |
| | | Au | 25 000 | 19 000 | $8.4 \times 10^{6}$ |
| $2N_2O \longrightarrow 2N_2 + O_2$ | 58 500 | Au | 29 000 | 29 500 | $5.9 \times 10^{9}$ |
| | | Pt | 32 500 | 26 000 | $2.1 \times 10^{9}$ |
| $2NH_3 \longrightarrow N_2 + 3H_2$ | 78 000 | W | 39 000 | 39 000 | $1.6 \times 10^{14}$ |
| | | Mo | 32 000-42 000 | 36 000 | $1.3 \times 10^{13}$ |
| | | Fe | 38 000-42 000 | 36 000 | $1.3 \times 10^{13}$ |
| | | Os | 47 000 | 31 000 | $1.9 \times 10^{11}$ |
| $CH_4 \longrightarrow C + 2H_2$ | 80 000 | Pt | 55 000-60 000 | 20 000 | $1.9 \times 10^{7}$ |
| $2SO_2 + O_2 \longrightarrow 2SO_3$ | 60 000 | Pt | 15 000 | 45 000 | $2.6 \times 10^{16}$ |
| | | Pd | 22 000 | 28 000 | $1.6 \times 10^{10}$ |

The last column gives values of $e^{\Delta E/RT}$ calculated for 600 K. It follows from these data that as a result of the reduction of the activation energy, heterogeneous catalysts increase the rate of a reaction

[1] It must be noted in passing that nothing can be said a priori on the relation between the activation energy of the non-catalytic reaction $E$ and the true activation energy $E_{tr}$. The quantity $\Delta E$ is the difference between the values of $E$ and the apparent activation energy, which actually determines the rate of a heterogeneous process.

$10^6$ to $10^{16}$ times. The specific nature of the action of the catalysts and their chemical nature have a quite clear influence—the value of $\Delta E$ differs for different catalysts and, naturally, the accelerating action of these catalysts is different.

It also follows from the above that if the products of a catalytic and a non-catalytic reaction are identical, the values of the heats of reaction also coincide.

7. *Appraisal of Catalyst Activity.* Table 12.7 compares the activation energies and relative rates of decomposition of formic acid on different catalysts. The activation energy changes insignificantly, not in agreement with the activity, and at any rate the difference in the activities of catalysts cannot be explained by the change in the activation energy.

TABLE 12.7

**Activation Energies and Rate of Reaction of Decomposition of Formic Acid $HCOOH \rightarrow H_2O + CO$ on Selected Catalysts at 300 °C**

| Catalyst | $E$, cal/mol | Relative rate |
|---|---|---|
| Glass | 24 500 | 1 |
| Au | 23 500 | 40 |
| Ag | 31 000 | 40 |
| Pt | 22 000 | 2 000 |
| Rh | 25 000 | 10 000 |

If we rewrite Eq. (12.59) for application in comparing the activity of two catalysts, using the subscripts "1" and "2" for denoting their properties, we get

$$\frac{k_1}{k_2} = \frac{C_1}{C_2} e^{(E_2-E_1)/RT} = \frac{C_1}{C_2} e^{\Delta E/RT} \tag{12.59a}$$

Applying this equation, for example for catalysis on rhodium and glass, we get

$$10\,000 = \frac{C_{Rh}}{C_{glass}} e^{500/1.987\times 573}$$

or

$$\frac{C_{Rh}}{C_{glass}} = 10\,000 e^{0.44} = 1.55 \times 10^4$$

Thus, owing to the change in the activation energy, the rate should decrease one-and-a-half times, and the entire acceleration effect should completely depend on the ratio of the preexponential factors $C_1/C_2$.

The first requirement to an appraisal of the activity of a catalyst is the necessity of doing this through a kinetic equation giving the

value of the rate constant—the most reliable index of activity. Any other methods of appraisal—through the amount of substance that has reacted during a definite time, according to the degree of transformation[1]—are ambiguous and may lead to serious misunderstandings.

Knowing the rate constant, we can calculate the efficiency of a catalyst, i.e. the number of molecules or moles (or any other quantity proportional to them) that has reacted in a unit of time (for example, in one second or one minute) at stationary concentrations of the reactants (for example, unit ones). But even when reliable kinetic data have been obtained and the efficiency has been found, the quantity of catalyst which the value of the efficiency obtained should be related to remains unclear. In homogeneous processes the catalyst is discrete to molecular dimensions, and its activity is directly proportional to the acting mass. In heterogeneous catalysis the catalyst acts only with its surface, and the latter is far from being in a single-valued relationship with the total mass. Hence two different ways of appraising the activity appear, the activity per unit of mass and that per unit of catalyst surface.

By the *total activity* or the *mass efficiency* $A$ of a catalyst is meant the amount of a substance (in moles) that reacts in a unit of time under the action of a unit of mass of the catalyst, i.e. its dimension is mol/g·s.

The *specific activity* $a$ of a catalyst is the amount of a substance (in moles) that reacts in a unit of time per unit of surface area of the catalyst, i.e. its dimension is mol/m$^2$·s.

It is quite clear from what has been said that different results are obtained when using these quantities.

Let us consider, for example, the experimental data obtained by G. Boreskov in studying the specific activity of metals catalyzing deutero-hydrogen exchange:

$$H_2 + D_2 \rightleftharpoons 2HD$$

Table 12.8 gives the activities of three nickel catalysts prepared in different ways and having a surface area differing by more than 150 times. If our appraisal is based on the total activity $A$, the catalysts will be arranged as follows in the order of decreasing activities:

$$A_{NiO} > A_{Ni\text{-}Al} > A_{Ni(CO)_4}$$

If we compare the specific activities $a$, we get

$$a_{NiO} > a_{Ni(CO)_4} > a_{Ni\text{-}Al}$$

[1] There is a special danger when the degree of transformation is high and is close to the equilibrium value. It is owing to the failure to take this circumstance into account that the heats of reaction were sometimes taken as the activation energy.

TABLE 12.8

**Catalytic Activity of Differently Prepared Nickel Catalysts at 100 °C for Deutero-Hydrogen Exchange**

$$H_2 + D_2 \rightleftharpoons 2HD$$

| Way of preparing catalyst | $A$, mol/g·s | $A_s$, m²/g | $a = A/A_s$, mol/m·s |
|---|---|---|---|
| Reduction of NiO | 3.1 | 12 | 0.25 |
| Thermal decomposition of $Ni(CO)_4$ | 0.039 | 0.31 | 0.125 |
| Leaching of alloy Ni-Al | 2.7 | 50 | 0.055 |

It is naturally more logical to compare catalysts according to their specific activity. The specific activities of nickel prepared in different ways, however, differ (in the present example they differ by about five times). For this reason the question appears on the cause of this difference and on how it can affect the appraisal of activity.

It is possible that not all the atoms of the surface are active to the same extent, and only some of them, the so-called *active centres*, have the ability of forming active intermediates. The number of active centres may depend on the way the catalyst is prepared. If this is true, then the preexponential factor in Eq. (12.58) is directly related to the number of active centres of a heterogeneous catalyst.

**12.9. Activated Adsorption.** The rates of the process of adsorbing different substances on different adsorbents change within broad limits. Gases and vapours may be adsorbed either very rapidly or at a measurable rate. In physical adsorption the amount of adsorbate decreases with a growth in the temperature at constant pressure. The rate of physical adsorption depends only slightly on the temperature, since it is mainly determined by the rate of diffusion. In chemisorption the amount of adsorbate also decreases with a growth in the temperature, but the amount of a chemisorbed substance usually exceeds that of a physically adsorbed one, while the rate of the process appreciably depends on the temperature (it grows according to an exponential law with a growth in the temperature) and is characterized by a definite and considerable activation energy (of the order of tens of thousands of cal/mol). Chemical adsorption of this type (at elevated temperatures) has been called *activated.*

Very frequently both types of adsorption can be observed for the same substance, but within different temperature intervals. At low temperatures physical adsorption occurs, and at high ones activated adsorption. Both processes are usually separated by an intermediate region (see, for example, Fig. 12.10) characterized by an increase in the amount of the adsorbate with the temperature. Thus, platinum

at 20 °C adsorbs about ten times more oxygen than at —175 °C. The adsorption of hydrogen on copper decreases at temperatures from 70 to 100 K, then grows with the temperature. It reaches a maximum at 450 K and then drops again. Figure 12.10 shows the adsorption of hydrogen on manganese and chromium oxide catalysts. The activation energy measured in the region of activated adsorption is frequently of the same order as the activation energy of the reaction between a free radical with a molecule. This allows us to assume

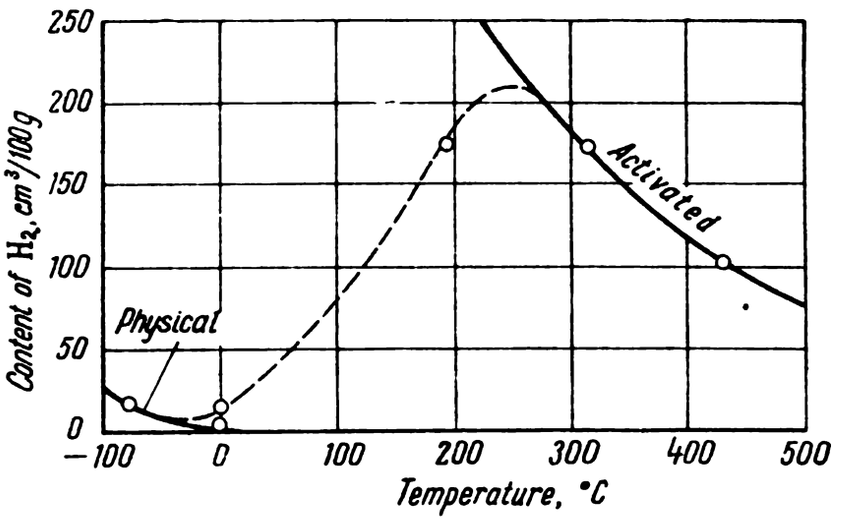



Fig. 12.10. Isobar of hydrogen adsorption on catalyst $MnO_2 + Cr_2O_3$

that the process of activated adsorption is similar to the reaction between an atom and a molecule in the gaseous phase, since there are always not occupied active sites on the surface of the adsorbent. It is quite possible that activated adsorption is due to stretching of the molecules on the surface of the adsorbent, which sometimes leads to their dissociation into atoms. Ideas of activated adsorption were advanced by H. Taylor back in 1931, but to date these ideas do not have a sufficiently good experimental background. The question of the mechanism of activated adsorption is still being discussed in chemical literature. Some authors ascribe the activation energy (calculated according to the change in the rate of adsorption) to processes of solution, diffusion, migration or to a reaction on the surface, and not to the process of chemisorption itself.

In a number of cases the optimal temperatures for conducting heterogeneous catalytic reactions coincide with the range of temperatures of activated adsorption. For example, the temperatures of the process of ammonia synthesis coincide with those of activated adsorption of nitrogen. As shown by experiments with nitrogen isotopes, a molecule of nitrogen in activated adsorption does not break up into atoms. Although the isotopic exchange $N_2^{14} + N_2^{15} \rightarrow 2N^{14}N^{15}$ does proceed on the catalyst at the temperatures of the process, its rate is considerably slower than that of the synthesis itself. Such

an exchange can proceed only as a result of rupture of the bonds in the nitrogen molecules. Since this is a slow process, it cannot affect the faster process of ammonia synthesis. Consequently nitrogen atoms do not participate in the synthesis reaction. The rate of the process of activated adsorption of nitrogen which does not result in dissociation of the nitrogen molecules into atoms coincides with the rate of the reaction of ammonia synthesis.

Although activated adsorption is sometimes one of the steps of a heterogeneous catalytic process, its role in the latter is nevertheless insufficiently clear. It may be assumed that activated adsorption leads to deformation of the adsorbed molecules and thus increases their reactive properties. Besides, the energy of dissociation of the molecules adsorbed is found to be smaller than the energy of dissociation of the molecules in the bulk.

**12.10. Kinetically- and Diffusion-Controlled Heterogeneous Catalytic Processes.** A heterogeneous chemical reaction may proceed only with continuous molecular or convective diffusion of the reactants to the surface on which the given reaction is proceeding, and also with continuous reverse diffusion of the products.

The rate of a process as a whole will be determined by the rate of its slowest step. If the rate of a reaction on the surface of a catalyst is greater than that of diffusion, the rate of the process as a whole will be determined by the rate of diffusion. The observed macroscopic kinetics of the reaction will obey equations that can be obtained by considering only processes of diffusion and, consequently, will not reflect the true rate of the chemical reaction on the surface of the catalyst. In this case it is said that the process is a *diffusion-controlled* one. It is most frequently described by a first-order reaction equation, since the rate of diffusion is directly proportional to the concentration.

If the rate of the chemical reaction is considerably slower than that of diffusion, the rate of the process as a whole will be determined by that of the chemical reaction. Here the process is a *kinetically-controlled* one and is described by an equation of the kinetics of the reaction that proceeds on the surface of the catalyst.

If the rate of diffusion and that of the chemical reaction, when considered independently of each other, are commensurable, we have a process that is intermediate between a kinetically- and diffusion-controlled one.

The same process, depending on the conditions which it is conducted in, may be kinetically- or diffusion-controlled. The nature of a heterogeneous process is greatly affected by its temperature, the pressures of the reactants, the rates of flow, and the porosity of the catalyst.

When the temperature changes by 10 K, the rate of diffusion, as shown by experiments, changes approximately 1.2 times, while the

rate of the chemical reaction changes three or four times. For this reason when the temperature is reduced, the rate of the chemical reaction will decrease faster than the rate of diffusion, and at low temperatures the process more frequently is a kinetically-controlled one.

A typical dependence of the logarithm of the rate constant of a heterogeneous process on the inverse temperature is shown in Fig. 12.11. Section *AB* of the curve for a practically constant value of *k* (*k* does not depend on the temperature) corresponds to a diffusion-controlled process. Section *CD* corresponds to a kinetically-controlled process. This section is usually characterized by a considerable value of the activation energy. Section *BC* corresponds to transition conditions. Generally the transitions between diffusion- and kinetically-controlled processes and vice versa are not so sharp as shown in the figure and are described by a smooth curve. Such a curve is observed for porous catalysts. There is practically no transition zone on curves characterizing non-porous surfaces. At point *B* the curve sharply changes its direction (*BE*), characterizing a kinetically-controlled process.

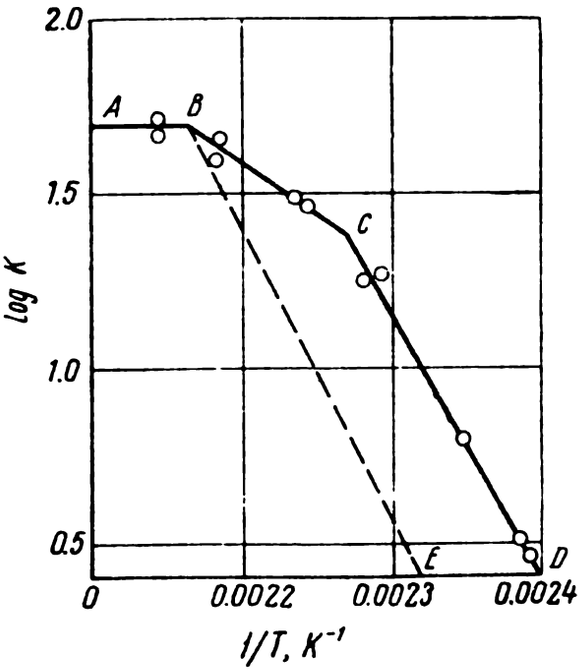



Fig. 12.11. Dependence of logarithm of apparent rate constant on inverse temperature for reaction of oxidation of acetylene on manganese peroxide promoted by silver

To determine theoretically how a process is controlled, it is necessary to appraise the rates of diffusion and of the chemical reaction separately as those of independent processes. The ratio between the rates determined in this way indicates how the process as a whole is controlled. This should be done because with a stationary course of a reaction the rate of diffusion becomes equal to that of the reaction regardless of the conditions of the process, i.e. this equality is observed in kinetically-, diffusion-controlled and intermediate processes. In the stationary course of a reaction the term *diffusion-controlled* does not at all mean, consequently, that the actual rate of the reaction on the reaction surface is greater than the rate of diffusion to this surface. Both rates are equal, but owing to the slow influx of the substances to the surface, the rate of the chemical reaction on the surface is forced to become equal to the rate of diffusion. The concentration of the substance on the surface is low, and the gradient of concentration near the surface is great. Conversely, in a kinetically-controlled process, where the independently determined rate of diffusion considerably exceeds the rate of the reaction, the rates of diffusion and of the reaction are equal at only slightly differing values of the concentrations of the reactants in the bulk and on the surface.

The rate of diffusion $J_1$ is directly proportional to the gradient of concentration $c - c_1$ (where $c$ is the concentration of the substance in the bulk, and $c_1$

on the surface), i.e.

$$J_1 = \beta (c - c_1) \tag{12.60}$$

where $\beta$ is the diffusion rate constant, which is a function of the coefficient of diffusion. Its exact value can be obtained by solving an equation compiled on the basis of Fick's first law for a given specific case.

The rate of the chemical reaction $J_2$ is a function of the concentration of the substance on the surface, i.e.

$$J_2 = f (c_1) \tag{12.61}$$

In a stationary state both these rates should be equal, i.e.

$$f (c_1) = \beta (c - c_1) \tag{12.62}$$

In the simplest case, when the reaction on the surface proceeds as a first-order one

$$J_2 = f (c_1) \doteq kc_1 \tag{12.63}$$

Inserting Eq. (12.63) into Eq. (12.62), we get

$$kc_1 = \beta (c - c_1) \tag{12.64}$$

Hence

$$c_1 = \frac{\beta c}{k+\beta} \tag{12.65}$$

Inserting Eq. (12.65) into Eq. (12.63), we find that for a stationary state

$$J_2 = \frac{k\beta}{k+\beta} c \tag{12.66}$$

Thus, in these conditions the macroscopic rate of the reaction also corresponds to the rate of a first-order reaction with respect to the concentration of the reactant, i.e.

$$J_2 = k_1 c \tag{12.67}$$

where $k_1 = \dfrac{k\beta}{k+\beta}$

or

$$\frac{1}{k_1} = \frac{1}{k} + \frac{1}{\beta} \tag{12.68}$$

This equation shows that if a reaction on a surface proceeds as a first-order one, the reciprocals of the rate constants of the reaction on the surface and of the rate of diffusion are summated.

When $k \gg \beta$, the process will be a diffusion-controlled one, and

$$k_1 \approx \beta \tag{12.69}$$

According to Eq. (12.65)

$$c_1 = \frac{\beta}{k} \tag{12.70}$$

and since according to the condition we have $k \gg \beta$, then from the last expression it follows that

$$c_1 \ll c \tag{12.71}$$

This relation between the concentrations in the bulk and on the surface is characteristic of a diffusion-controlled process.

If $k \ll \beta$, then $k_1 \approx k$ and $c_1 \approx c$, which corresponds to a kinetically-controlled reaction.

Such simple relations between the constants of a process are obtained only for first-order reactions. For other orders of a reaction, the relations between the constants are more complicated. If the order of a reaction proceeding on a surface is $m$, then on the basis of what has been said above we have

$$kc_1^m = \beta (c - c_1) \tag{12.72}$$

Solution of this equation relative to $c$ gives

$$c = \frac{k}{\beta} c_1^m + c_1 \tag{12.73}$$

On the other hand

$$kc_1^m = k_1 c^n \tag{12.74}$$

where $k_1$ and $n$ are the apparent rate constant and order of a reaction, respectively, determined according to the change in the concentration of the reactants in the bulk above the reaction surface. It follows from Eq. (12.74) that

$$\frac{1}{k_1} = \frac{c^n}{c_1^m k} \tag{12.75}$$

Inserting Eq. (12.73) into Eq. (12.75), we get

$$\frac{1}{k_1} = \frac{\left(\frac{k}{\beta} c_1^m + c_1\right)^n}{c_1^m k} \tag{12.76}$$

When $n = m = 1$ we get the already known equation

$$\frac{1}{k_1} = \frac{1}{\beta} + \frac{1}{k} \tag{12.77}$$

It can be seen that for all reactions whose order is higher than the first one, the relation between the constants is very complicated.

If not all the sections of a surface on which a reaction proceeds are accessible for the reacting molecules to an equal degree, the reaction is frequently found to be kinetically-controlled on part of the surface and diffusion-controlled on the remaining part. The outer surface of a solid catalyst is the most accessible part, and the surface of its pores is the least accessible one. This is why a reaction which is kinetically-controlled on the outer surface and diffusion-controlled inside the pores is said to be an internal diffusion-controlled one.

In general, when a reaction is conducted on a surface whose parts are not equally accessible, four limiting cases are possible.

1. An external diffusion-controlled process. Here the concentration of the reactants even on the surface of a porous body, and moreover inside the pores is much lower than in the bulk. The kinetics of the process obeys equations of diffusion.

2. An internal diffusion-controlled process. In such conditions the concentrations of the reactants at the outer surface of a porous catalyst are quite close to those in the bulk, while the concentrations in the pores decrease from the outer surface of the grains to their centre. The concentrations of the products grow in this direction.

The kinetics of the process depends on the ratio between the outer and inner surfaces. If they are commensurable, the kinetics of the reaction corresponds to a process that is intermediate between a kinetically- and diffusion-controlled one.

3. An external kinetically-controlled process. Here the concentrations of the reactants on the surface of the catalyst and in the bulk are equal, but the reaction proceeds only on the outer surface of the catalyst. The kinetics of the process is determined by that of the chemical reaction.

4. An internal kinetically-controlled process. In such conditions the concentrations of the reactants in the bulk, on the surface of the catalyst and inside the pores are identical. The kinetics of the process as a whole is also determined by that of the chemical reaction.

For the external kinetically-controlled processes, the rate of the process depends on the magnitude of the outer surface of the catalyst, and for the internal ones—on the entire surface of the catalyst (the outer surface of the catalyst and the inner one—the surface of the pores accessible for the molecules of the reactant).

**12.11. Kinetics of Heterogeneous Catalytic Reactions in Static Conditions.** We shall consider two cases of heterogeneous catalytic reactions on a solid catalyst in which the reactants and products are gaseous.

1. *Kinetics of Processes in Which One Substance Reacts and the Products Do Not Inhibit the Process.* Examples of such reactions are the reactions of decomposition of some substances, such as $NH_3$ on platinum, and methane on carbon.

As indicated above, in a typical heterogeneous process only those substances react that are adsorbed on a surface. The rate $J$ of a heterogeneous chemical reaction is determined as the amount of substance reacting in a unit of time on a unit of surface area of the catalyst, i.e.

$$J = \frac{dx}{A\,dt} \tag{12.78}$$

where $x$ = amount of substance that has reacted by the moment $t$, in moles

$A$ = total surface area of catalyst on which the chemical process proceeds.

The rate of a heterogeneous chemical process, according to the main postulate of chemical kinetics, is directly proportional to the surface concentration of the substances. The latter quantity is directly proportional to the fractional coverage of the surface $\theta$ (see Vol. 1, Sec. 16.3). Hence we can write that

$$\frac{dx}{A\,dt} = k'\theta \tag{12.79}$$

Since the surface of a given catalyst is constant, the magnitude of the total surface area of the catalyst can be introduced into the rate constant of the process $k'$, i.e. we can assume that

$$k'A = k \tag{12.80}$$

For this reason Eq. (12.79) can be written in a simpler form:

$$\frac{dx}{dt} = k\theta \tag{12.81}$$

The magnitude of the surface occupied by the reactant per square centimetre of the catalyst surface area can be found on the basis of Langmuir's adsorption theory (see Vol. 1, Sec. 16.4):

$$\theta = \frac{Kp}{1+Kp} \tag{12.82}$$

Equation (12.82) can be deduced on the basis of the kinetics of the adsorption process if we adopt the following simplifying assumptions: (1) no forces of attraction or repulsion act between the adsorbed molecules; (2) the process of adsorption terminates when all the adsorption (active) centres or sites on the surface of a solid (or liquid) are occupied; in other words, the process of adsorption terminates when a layer one molecule thick (a completed monolayer) is formed at the interface between phases, and (3) all the adsorption centres are the same in all respects. On the basis of these assumptions we can consider that the rate $J_1$ of an adsorption process is directly proportional to the pressure $p$ of the gas and the free surface area of the solid (catalyst) $1 - \theta$, i.e.

$$J_1 = k_1 p\,(1 - \theta)$$

where $k_1$ is a constant characterizing the rate of adsorption.

The rate $J_2$ of the reverse process (desorption) is directly proportional to the surface area occupied by the reacting molecules, i.e.

$$J_2 = k_2\theta$$

where $k_2$ is a constant characterizing the rate of desorption. At the moment of equilibrium the rates of both opposite processes should be the same:

$$J_1 = J_2$$

Equating the values of these quantities, we get

$$k_1 p\,(1 - \theta) = k_2\theta$$

Solution of this equation relative to $\theta$ yields

$$\theta = \frac{k_1 p}{k_2 + k_1 p}$$

Dividing the numerator and denominator by $k_2$ and designating $k_1/k_2$ by $K$, we have

$$\theta = \frac{Kp}{1+Kp}$$

where $p$ = pressure of the gas
$K$ = adsorption equilibrium constant (*adsorption coefficient*).

It follows from Eq. (12.82) that if adsorption is slight, then $\theta \ll 1$, and, therefore, $K \ll 1$. Hence the quantity $Kp$ in the denominator of Eq. (12.82) may be neglected, and Eq. (12.82) becomes

$$\theta = Kp \tag{12.83}$$

i.e. at low pressures the surface area occupied by the adsorbate is directly proportional to the pressure. This region has been named the region of linear adsorption. If adsorption is great, then $Kp \gg 1$, and we can neglect the figure 1 in the denominator of Eq. (12.82), which now becomes

$$\theta = 1 \tag{12.84}$$

This equation is that of the asymptote of the curve described by Eq. (12.82).

Using Eq. (12.82) and Eqs. (12.83) and (12.84) following from it, we can get convenient equations for calculations of the kinetics of heterogeneous reactions for limiting cases.

If one substance reacts and its adsorption is low, then inserting into Eq. (12.81) the value of $\theta$ from Eq. (12.83), we get

$$\frac{dx}{dt} = kKp \tag{12.85}$$

If we introduce the notation

$$kK = k^{\star} \tag{12.86}$$

then Eq. (12.85) becomes

$$\frac{dx}{dt} = k^{\star}p \tag{12.87}$$

It is quite obvious that in the given case the equation of the kinetics of a heterogeneous reaction corresponds to that of a first-order one, since the concentration of the reactant expressed through its partial pressure $p$ enters into the expression to the first power.

To integrate Eq. (12.87), the partial pressure of the reactant should be expressed in terms of the number of gramme-molecules using Dalton's law and Clapeyron's equation, namely,

$$p = \frac{n_t}{V} RT = \frac{n_0 - x}{V} RT \tag{12.88}$$

where $n_t = n_0 - x$ = number of gramme-molecules of the reactant at the moment $t$

$n_0$ = number of gramme-molecules of the reactant at the initial moment

$V$ = total volume of the system.

Inserting Eq. (12.88) into Eq. (12.87), we get an expression that is convenient for integration. The total volume $V$ of the system is a constant quantity, since a process in static conditions is usually

conducted at a constant volume. The transition from partial pressures to the numbers of reacting gramme-molecules, as can be seen from the example considered above, is very simple, and for this reason we shall omit this transformation in the following.

The constant $k^\star$ in the equations of the kinetics is called the *apparent rate constant* of a process. As can be seen from Eq. (12.86), it is the product of the true rate constant of a chemical reaction $k$ and the adsorption coefficient $K$.

Examples of reactions whose kinetics obeys Eq. (12.87) are the reactions of decomposition of hydrogen arsenide $AsH_3$ and hydrogen phosphide $PH_3$ on glass, the decomposition of nitrogen dioxide $NO_2$ on gold, hydrogen iodide on platinum and methane on carbon.

Inserting Eq. (12.82) into Eq. (12.81), we get

$$\frac{dx}{dt} = k^\star \frac{p}{1+Kp} \tag{12.89}$$

where $k^\star = kK$ is the apparent rate constant of a reaction. This expression describes processes in which the reactant is adsorbed moderately. It can be approximately written as follows:

$$\frac{dx}{dt} = k^\star p^{1/n} \tag{12.90}$$

It can be seen that a fractional order is obtained for such a reaction, equal to $1/n$ (where $n > 1$). Such a fractional order is an apparent one. The true order of a reaction proceeding on the surface of a catalyst is the first one. The apparent order is obtained because in accordance with the method of calculations which we have adopted, quantities are introduced into the kinetic equation that characterize the change in the concentration of the substance not directly on the surface, but in the bulk. Our expression contains not the surface concentration, which is characterized by the quantity $\theta$, but a quantity characterizing the content of the reactant in the bulk—its partial pressure $p$. The surface concentration, which is proportional to the quantity $\theta$, enters into the equation of the kinetics (12.81) to the first power, and, consequently, the true order of the reaction is the first one. An example of a reaction with a fractional apparent order is the reaction of decomposition of ammonia on arsenic.

If the reactant is greatly adsorbed, then $\theta = 1$, and, inserting Eq. (12.84) into Eq. (12.81), we get

$$\frac{dx}{dt} = k \tag{12.91}$$

It is obvious that the apparent order of a reaction will be equal to zero, i.e. it can be assumed that the partial pressure of the reactant enters into this equation to the zero power ($p^0 = 1$). In addition, it can be seen that in contrast to Eqs. (12.87), (12.89) and (12.90), equation (12.91) contains the true rate constant of a process.

It should be noted that the apparent order of heterogeneous reactions may change for the same reaction from the zero one, if the reaction is conducted under a high pressure, through a fractional variable order to the first one if the pressure of the reactant becomes very low. This is quite understandable if we remember the corollaries following from Eq. (12.82), which determines the fraction of the surface occupied by the reactant.

2. *Kinetics of Processes in Which One Substance Reacts and the Products Inhibit the Process.* In the processes considered above, the products did not inhibit the process itself. Now let us consider the kinetics of processes into which complications are introduced by inhibition by the products. The latter may be adsorbed on the surface of the catalyst and thus reduce the surface area occupied by the reactant. This will obviously lead to inhibition of the process. For this reason when calculating the surface area covered by the reactant, account should be taken of adsorption of the products of the reaction. For simplicity we shall consider processes in which only one product is adsorbed and, consequently, inhibits the process. The calculation of the kinetics of a process which is inhibited by several products is in principle the same, as will be shown below.

If two substances A and B are adsorbed, we can write (see Vol. 1, Sec. 16.4) that

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \tag{12.92}$$

$$\theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B} \tag{12.93}$$

where $K_A$ and $K_B$, $p_A$ and $p_B$ are the respective adsorption coefficients and partial pressures of substances A and B. It should be noted that Eq. (12.93) can be obtained on the basis of assumptions as has been done above.

If only one substance reacts and the reaction on a surface follows an equation of the first order (the true order), then the equation of the kinetics of a chemical process can be written as

$$\frac{dx}{dt} = k\theta_A \tag{12.94}$$

Let us consider several examples of calculations based on the use of Eq. (12.92).

1. The reacting gas is adsorbed poorly, and the product moderately. It follows from these initial conditions that $K_A p_A \ll 1$, therefore this product may be neglected in the denominator of Eq. (12.92), i.e.

$$\theta_A = \frac{K_A p_A}{1 + K_B p_B} \tag{12.95}$$

Inserting Eq. (12.95) into Eq. (12.94), we get

$$\frac{dx}{dt} = k^{\star} \frac{p_A}{1+K_B p_B} \tag{12.96}$$

where $k^{\star} = kK_A$ is the apparent rate constant of the reaction.

An example of a reaction whose kinetics obeys Eq. (12.96) is the reaction of decomposition of nitrous oxide $N_2O$ on platinum. The process of decomposition is inhibited by the oxygen.

2. The reactant is adsorbed poorly, and the product greatly. In this case, according to what has been said above, $K_A p_A \ll 1$ and $K_B p_B \gg 1$. Consequently, the figure one and the quantity $K_A p_A$ may be neglected in the denominator of Eq. (12.92) as being very small in comparison with the quantity $K_B p_B$. Equation (12.92) will be written as

$$\theta_A = \frac{K_A p_A}{K_B p_B} \tag{12.97}$$

Inserting Eq. (12.97) into Eq. (12.94), we get

$$\frac{dx}{dt} = k^{\star} \frac{p_A}{p_B} \tag{12.98}$$

where $k^{\star} = k \frac{k_A}{k_B}$.

An example of such a process is the decomposition of ammonia on platinum. The process is inhibited by the hydrogen formed, which is greatly adsorbed by the surface of the platinum.

3. The reactant and the product are adsorbed greatly. Here $K_A p_A \gg 1$ and $K_B p_B \gg 1$. We may neglect the figure one in the denominator of Eq. (12.92), consequently

$$\theta = \frac{K_A p_A}{K_A p_A + K_B p_B} \tag{12.99}$$

Inserting Eq. (12.99) into Eq. (12.94), we get

$$\frac{dx}{dt} = k^{\star} \frac{p_A}{K_A p_A + K_B p_B} \tag{12.100}$$

where $k^{\star} = kK_A$.

An example of such a reaction is that of dehydration of ethyl alcohol on aluminium oxide. The process is very greatly inhibited by the water formed.

It is just as simple to obtain the equations of the kinetics of heterogeneous chemical reactions if two substances react. If two reactants are adsorbed on the same adsorption centres and the true order of the reaction is the second one, then the general equation of its kinetics can be written as follows:

$$\frac{dx}{dt} = k\theta_A \theta_B \tag{12.101}$$

The values of $\theta_A$ and $\theta_B$ in this case can be found from Eqs. (12.92) and (12.93).

**12.12. True and Apparent Activation Energies of Heterogeneous Chemical Reactions.** If we use experimental data to construct a diagram showing how the apparent rate constant of a heterogeneous chemical reaction depends on the inverse temperature, we get a straight line similar to that described by the Arrhenius equation. The equation corresponding to this straight line can be written in the same way as the Arrhenius equation

$$\ln k^* = -\frac{E^*}{RT} + \ln C \tag{12.102}$$

or, if this equation is differentiated with respect to the temperature, we get

$$\frac{d \ln k^*}{dT} = \frac{E^*}{RT^2} \tag{12.103}$$

The quantity $E^*$ in this equation is called the *apparent activation energy*. There is a simple relation, which can be easily found, between the apparent and true activation energies of a heterogeneous chemical reaction.

Let us consider the method of finding this relation on the example of a reaction with the participation of one slightly adsorbed gas, the product not inhibiting the process. According to Eq. (12.86), the apparent rate constant will be

$$k^* = kK \tag{12.104}$$

The adsorption coefficient (equilibrium constant) $K$ is equal to the ratio between the rate constants of the processes of adsorption and desorption, i.e.

$$K = \frac{k_1}{k_2}$$

Inserting this ratio into the equation for the apparent rate constant of a chemical process, we get

$$k^* = k\frac{k_1}{k_2} \tag{12.105}$$

Each of the constants entering into Eq. (12.105) is a function of the temperature. It is known from the kinetic deduction of the Langmuir equation for an adsorption isotherm that $k_1$ is inversely proportional to the square root of the temperature, namely,

$$k_1 = C'/\sqrt{T} \tag{12.106}$$

where $C'$ is a constant quantity.

The constant $k_2$ characterizing the desorption process changes with the temperature in the same way as the saturated vapour pressure, i.e.

$$k_2 = C'' e^{-Q_a/RT} \tag{12.107}$$

where $C''$ = constant not depending on the temperature
$Q_a$ = heat of adsorption.

The rate constant of a chemical reaction changes with the temperature according to the Arrhenius equation, i.e.

$$k = Ce^{-E/RT} \tag{12.108}$$

The rate constant of an adsorption process $k_1$ changes very slightly with the temperature in comparison with $k$ and $k_2$ (owing to the small value of the change in $T^{1/2}$ with an increase in $T$). The temperature dependence of $k_1$ may be neglected, and this quantity may be considered as constant. Inserting Eqs. (12.108) and (12.107) into Eq. (12.105), we get

$$k^* = Ce^{-E/RT} \frac{k_1}{C\, e^{-Q_a/RT}} \tag{12.109}$$

Taking logarithms of this equation, we get

$$\ln k^* = -\frac{E}{RT} + \frac{Q_a}{RT} + \ln \text{const} \tag{12.110}$$

where const $= C \frac{k_1}{C'}$.

Differentiation of Eq. (12.110) with respect to $T$ yields

$$\frac{d \ln k^*}{dT} = \frac{E - Q_a}{RT^2} \tag{12.111}$$

Comparing Eq. (12.111) with Eq. (12.103), we see that

$$E^* = E - Q_a \tag{12.112}$$

Equation (12.112) characterizes the dependence of the apparent activation energy on the true one for the case being considered. A glance at Eq. (12.112) shows that the apparent activation energy is smaller than the true one by the value of the heat of adsorption of the reactant.

For the case when the reactant is adsorbed slightly and the product greatly, we can find in the same way that

$$E^* = E - Q_{a,A} + Q_{a,B} \tag{12.113}$$

where $Q_{a,A}$ and $Q_{a,B}$ are the heats of adsorption of substances A and B, respectively.

Thus, to calculate the true activation energies it is necessary to know the heats of adsorption of the reactants and products. It is

quite difficult to determine these quantities experimentally, and for this reason they are usually unknown. In addition, the values of the heat of adsorption appreciably depend on the fractional coverage of the surface (see Vol. 1, *Surface Phenomena. Adsorption*).

**12.13*. Kinetics of Heterogeneous Reactions in a Flow System.** The equations of the kinetics of heterogeneous chemical reactions proceeding in a flow system were derived by G. Panchenkov. For such a reaction, i.e. when the reactants flow in a tube through a stationary solid catalyst, in accordance with the definition given above (Sec. 12.11), its rate will be

$$J_A = \frac{JA_t\, dl}{dA} \tag{12.114}$$

where $J$ is the rate determined by the amount of substance reacting in a unit of time in a unit of volume. In Eq. (12.114) we multiply this quantity by an element of volume $A_t\, dl$ and divide it by an element of the surface area $dA$. This gives us the amount of substance that reacts in a unit of time per unit of surface area of the catalyst. Here $A_t$ is the cross-sectional area of the tube free of the catalyst. The quantity $dA$ corresponds to the area of the catalyst filling an element of the tube with a length of $dl$, i.e.

$$dA = A_0\, dl \tag{12.115}$$

where $A_0$ is the area of the catalyst per unit of length of the layer in the direction of flow.

Inserting Eqs. (1.164) and (12.115) into Eq. (12.114), we get for conditions of ideal displacement

$$J_A = \frac{n_{0,A_i}\, dx}{A_0\, dl} \tag{12.116}$$

In Eq. (12.116) we can replace the area $A_0$ per unit of length of the catalyst layer by the area $A_{0,V}$ per unit of catalyst volume. If we denote the total cross-sectional area of the tube by $A_t'$, the area $dA$ will obviously correspond to the volume $A_t'\, dl$ of the part of the tube filled by the catalyst, and since the area $A_{0,V}$ corresponds to a unit of volume of the catalyst, it follows from a simple proportion that

$$dA = A_{0,V} A_t'\, dl \tag{12.117}$$

Inserting Eq. (12.117) into Eq. (12.116), we get, with account of Eq. (12. 115)

$$J_A = n_{0,A_i} \frac{dx}{A_t' A_{0,V}\, dl} \tag{12.118}$$

But

$$A_t'\, dl = dV \tag{12.119}$$

where $V$ is the volume of the catalyst.

Hence, inserting Eq. (12.119) into Eq. (12.118), we get

$$J_A = n_{0,A_i} \frac{dx}{A_{0,V}\, dV} \tag{12.120}$$

It is general knowledge that for a kinetically-controlled heterogeneous reaction the amount of a substance reacting in a unit of time per unit of area of the catalyst is directly proportional to the fractions of this area occupied by the reactants raised to powers equal to the orders of the reaction. For this reason for

irreversible reactions having the order $n_i$ with respect to each substance we have

$$J_A = n_{0,A_i} \frac{dx}{A_{0,V} A_t' \, dl} = k' \theta_{A_1}^{\nu_1} \theta_{A_2}^{\nu_2} \ldots \theta_{A_n}^{\nu_n} \tag{12.121}$$

and for reversible ones

$$J_A = n_{0,A_i} \frac{dx}{A_{0,V} A_t' \, dl} = k_1' \theta_{A_1}^{\nu_1} \theta_{A_2}^{\nu_2} \ldots \theta_{A_n}^{\nu_n} - k_2' \theta_{A_1'}^{\nu_1} \theta_{A_2'}^{\nu_2} \ldots \theta_{A_n'}^{\nu_n} \tag{12.122}$$

where $\theta_{A_i}$ = surface occupied by reactant per unit of catalyst area
$\nu_i$ and $\nu_i'$ = orders of reaction with respect to each reactant and each product
$k_i'$ = rate constants of reactions.

Since the quantity $A_{0,V} A_t'$ is constant under given conditions, it can be introduced into the rate constant. For example, Eq. (12.121) can be written as

$$n_{0,A_i} \frac{dx}{dl} = k \theta_{A_1}^{\nu_1} \theta_{A_2}^{\nu_2} \ldots \theta_{A_n}^{\nu_n} \tag{12.123}$$

where $k = k' A_{0,V} A_t'$.

Let us consider several examples of heterogeneous gas reactions proceeding in a flow system in conditions of ideal displacement. Let one gas enter into reaction. The latter will hence be written in the general form as follows:

$$A \rightarrow \nu_1 A_1 + \nu_2 A_2 + \ldots + \nu_n A_n$$

The general equation of the kinetics of the process will be written in this case, according to Eq. (12.123), as follows:

$$n_{0,A} \frac{dx}{dl} = k \theta_A \tag{12.124}$$

Let us first consider cases when the products do not inhibit the reaction.

1. If adsorption of the reacting gas is slight, the surface covered by molecules of the reactant A will be determined by Eq. (12.83).

Expressing the partial pressure, according to Dalton's law, through the mole fraction and the total pressure $p$, we obtain

$$\theta_A = K_A \frac{1-x}{1+\beta x} p \tag{12.125}$$

where $\beta = \nu_1 + \nu_2 + \ldots + \nu_n - 1$
$x$ = mole fraction of reacted initial substance (reactant).

Inserting Eq. (12.125) into Eq. (12.124), we get

$$n_{0,A} \frac{dx}{dl} = k K_A \frac{1-x}{1+\beta x} p \tag{12.126}$$

This differential equation is solved by the method of separating variables. After separating variables we have

$$\frac{1+\beta x}{1-x} dx = \frac{k K_A p}{n_{0,A}} dl \tag{12.127}$$

Integration yields

$$k = \frac{n_{0,A}}{K_A p l} [-(1+\beta) \ln (1-x) - \beta x] \tag{12.128}$$

2. If the reacting gas is adsorbed moderately, then the area covered by the reactant is determined from Eq. (12.82). Since all the following reasoning is simple, to avoid repetition we shall immediately write the final form of the differen-

tial equation. To this end the partial pressures in the expression determining the area covered by the reactant should be expressed through the numbers of moles. To obtain the final form of the expression for the rate constant, we shall integrate the differential equation.

The differential equation for the case being considered will be

$$\frac{dx}{dl}=k\frac{K_{A}p}{n_{0,A}}\frac{1-x}{1+K_{A}p+(\beta-K_{A}p)x} \tag{12.129}$$

After integration we get

$$k=\frac{n_{0,A}}{K_{A}pl}\left[-(1-\beta)\ln(1-x)-(\beta-K_{A}p)x\right] \tag{12.130}$$

3. If adsorption of the reacting gas is great, the surface covered by the reactant is determined by Eq. (12.84) and, consequently, Eq. (12.124) becomes

$$\frac{dx}{dl}=\frac{k}{n_{0,A}} \tag{12.131}$$

whence after integration

$$k=\frac{n_{0,A}}{l}x \tag{12.132}$$

Let us consider the main cases when one gas reacts and the products inhibit the process. The basic kinetic equation retains the form of Eq. (12.124).

1. If adsorption of the reacting gas is slight, and of the products moderate, then

$$\theta_{A}=\frac{K_{A}p_{A}}{1+\sum(K_{A_i}p_{A_i})} \tag{12.133}$$

This equation differs from the previously derived Eq. (12.92) only in that its denominator contains the sum of the products of the adsorption coefficients and the partial pressures of all the participants of the reaction $\sum(K_{A_i}p_{A_i})$. This quantity enters into the equation because we are considering the more general case when any number of products (in the limit all the products) inhibit a process. Reasoning similar to the previous one, when we considered the adsorption of two substances, leads to Eq. (12.133). It is obtained by solving not two equations, but simultaneous equations whose number is equal to that of the gases being adsorbed.

Expressing the partial pressure through the total pressure and the number of moles, we get

$$\theta_{A}=K_{A}p\frac{1-x}{1+[\beta+\sum(K_{A_i}\nu_i)p]x} \tag{12.134}$$

Inserting Eq. (12.134) into Eq. (12.124), we have

$$\frac{dx}{dl}=k\frac{K_{A}p}{n_{0,A}}\frac{1-x}{1+[\beta+\sum(K_{A_i}\nu_i)p]x} \tag{12.135}$$

and after integration

$$k=\frac{n_{0,A}}{K_{A}pl}\left\{-\left[1+\beta+\sum(K_{A_i}\nu_i)p\right]\ln(1-x)-\left[\beta+\sum(K_{A_i}\nu_i)p\right]x\right\} \tag{12.136}$$

2. If the reactant gas is adsorbed poorly and the products greatly, the figure one can be neglected in the denominator of Eq. (12.133), and this equation beco-

mes

$$\theta_A = \frac{K_A p_A}{\sum (K_{A_i} p_{A_i})} \tag{12.137}$$

where $\sum (K_{A_i} p_{A_i})$ is the sum of the products of the adsorption coefficients and the partial pressures only for the products.

Inserting this expression into the general kinetic equation (12.124) and expressing the partial pressures through the numbers of moles, we get

$$\frac{dx}{dl} = k \frac{K_A}{n_{0,A} \sum (K_{A_i} \nu_i)} \frac{1-x}{x} \tag{12.138}$$

Integration yields

$$k = n_{0,A} \frac{\sum (K_{A_i} \nu_i)}{K_A l} [-\ln (1-x) - x] \tag{12.139}$$

This equation is obeyed by the kinetics of the reaction of cracking of separate hydrocarbons and their mixtures on alumino-silicate catalysts.

The reactions of catalytic cracking of hydrocarbons, like reactions of thermal cracking, are irreversible first-order ones. In the general form such a reaction can be written as follows:

$$A \rightarrow \nu_1 A_1 + \nu_2 A_2 + \ldots + \nu_n A_n$$

where A = pure reactant or mixture of reactants
$A_i$ = products of decomposition
$\nu_i$ = stoichiometric coefficients, which with the formula written in this way may be fractional.

As a result of cracking of hydrocarbons, high-molecular compounds and so-called coke are formed in addition to a gas and low-boiling products. The coke is a mixture of high-molecular hydrocarbons with a low hydrogen content which are greatly adsorbed on the surface of the catalyst. A reaction of catalytic cracking can therefore be considered as a heterogeneous chemical reaction of the first order characterized by weak adsorption of the reactants and great adsorption of some products. The rate of catalytic cracking obeys Eq. (12.139), but $\sum (K_{A_i} \nu_i)$ includes only quantities characterizing the substances that inhibit the process. Let us denote this sum by $B$. Equation (12.139) thus becomes

$$k = n_{0,A} \frac{B}{K_A l} [-\ln (1-x) - x] \tag{12.140}$$

This equation can be written as follows:

$$n_0 x = -n_0 \ln (1-x) - k \frac{K_A l}{B} \tag{12.141}$$

The equation will describe a straight line if we take $y = n_0 x$ and $z = -n_0 \ln (1 - x)$ as the variables. The section cut off by this line on the axis of ordinates gives the apparent rate constant of a reaction $k' = \frac{k K_A l}{B}$. Figure 12.12 shows $y = f(z)$ for the cracking of paraffin-base gas oil on two catalysts according to data of G. Panchenkov and E. Kuznetsova.

Equation (12.140) was found to hold for the cracking of separate hydrocarbons on synthetic alumino-silicate catalysts.

Figure 12.13 compares calculations according to Eq. (12.141) and experimental data for the reaction of cracking of the geometrical isomers of decalin obtained by G. Panchenkov and V. Krasavichev.

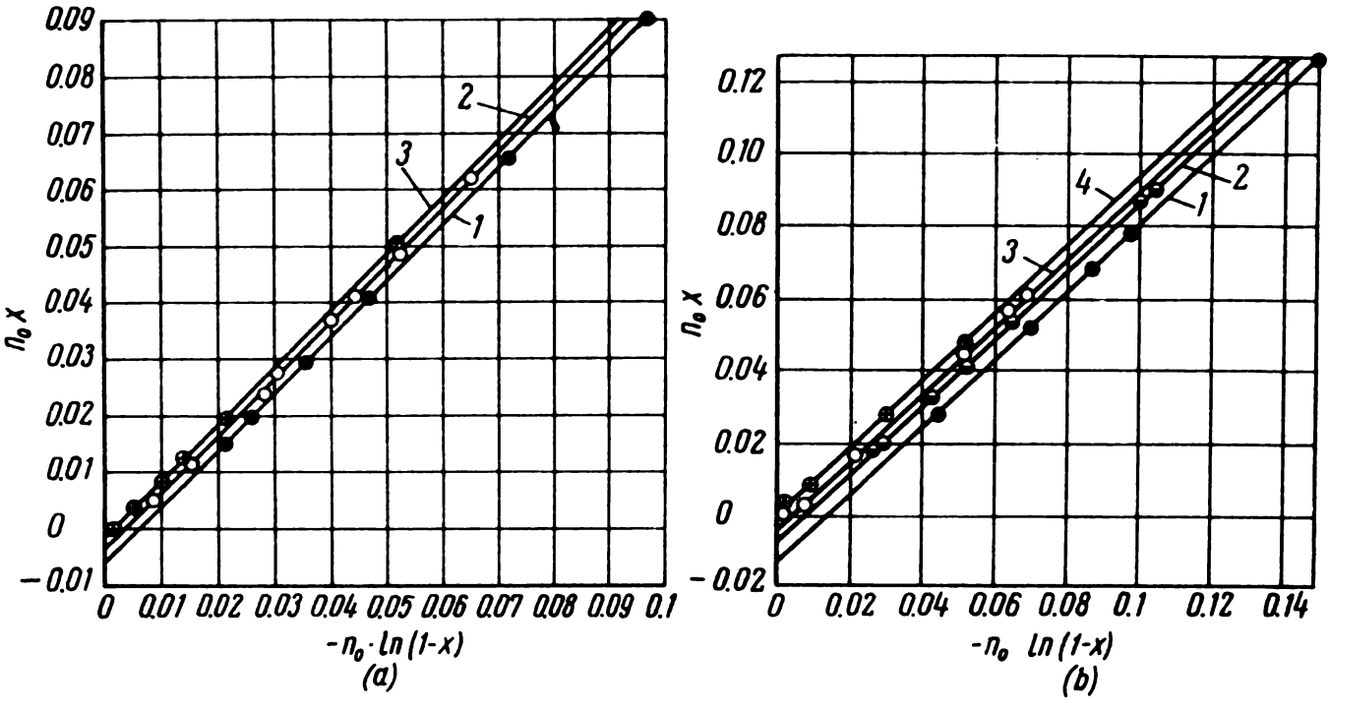



**Fig. 12.12. Kinetics of catalytic cracking of gas oil on alumino-silicate catalysts:**
*a*—5% $Al_2O_3$ + 95% $SiO_2$: *1*—at 490 °C; *2*—at 475 °C; *3*—at 450 °C; *b*—30% $Al_2O_3$ + + 70% $SiO_2$: *1*—at 490 °C; *2*—at 475 °C; *3*—at 450 °C; *4*—at 400 °C

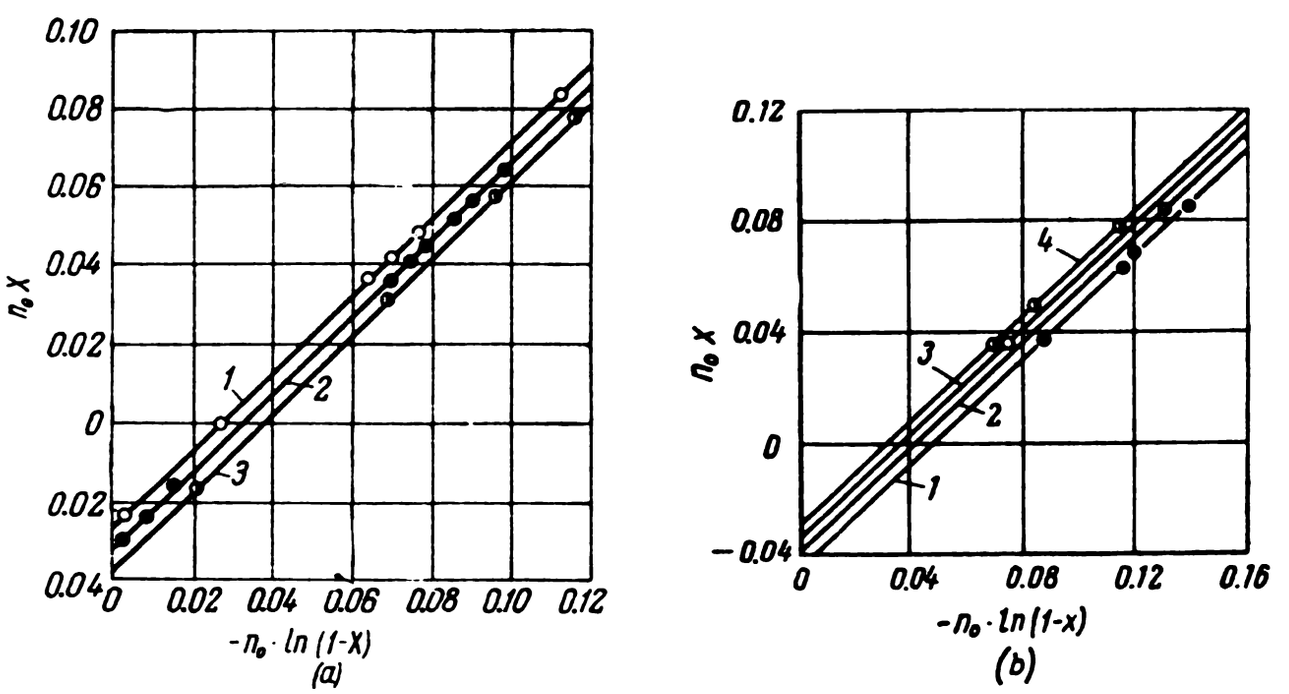



**Fig. 12.13. Kinetics of catalytic cracking of decalin isomers on alumino-silicate catalyst of the composition 30% $Al_2O_3$ + 70% $SiO_2$:**
*a*—*trans*-$C_{10}H_{18}$: *1*—at 470 °C; *2*—at 480 °C; *3*—at 490 °C; *b*—*cis*-$C_{10}H_{18}$: *1*—at 490 °C; *2*—at 480 °C; *3*—at 470 °C; *4*—at 460 °C

If we estimate the rate of a process not according to the total transformation, but according to the yield of intermediates, the reaction of cracking can no longer be considered as an irreversible first-order one. In this case it should be considered as a consecutive chemical reaction, since the low-boiling hydrocarbons formed decompose further into the products—gas and coke.

3. If the reacting gas and the products are greatly adsorbed, then according to Eq. (12.134) we have

$$\theta_A = \frac{K_A p_A}{K_A p_A + \sum (K_{A_i} p_{A_i})} \tag{12.142}$$

The differential equation of the rate of the chemical reaction in this case is

$$\frac{dx}{dl} = \frac{kK_A}{n_{0,A}} \frac{1-x}{K_A + [\sum (K_{A_i}\nu_i - K_A)]\, x} \tag{12.143}$$

Integration yields

$$k = \frac{n_{0,A}}{K_A l} \left\{ -\sum (K_{A_i}\nu_i) \ln (1-x) - [\sum (K_{A_i}\nu_i) - K_A]\, x \right\} \tag{12.144}$$

The equations for more complicated reactions with several reactants or that are reversible are solved in a similar way.

CHAPTER 13

# THEORY OF ACTIVE CENTRES IN HETEROGENEOUS CATALYSIS

**13.1. Active Centres of Heterogeneous Catalysts.** As experimental data on heterogeneous catalytic reactions accumulate, the question of the structure and nature of the active surface of the catalyst inevitably appears. In the early 1920's it became clear that only a small part of the entire surface of a catalyst participates in the acceleration of a reaction. This conclusion was reached on the basis of experimental results obtained in studying adsorption, the poisoning of catalysts, their sintering and certain other phenomena. Let us consider some of them.

1. *Adsorption Heterogeneity of Surface.* In Langmuir's adsorption theory a surface is assumed to be homogeneous, i.e. all its parts are considered to have identical adsorption potentials. The equation of the Langmuir adsorption isotherm, having the form

$$\theta = \frac{Kp}{1+Kp} \tag{13.1}$$

can be written as follows:

$$V = V_m \frac{Kp}{1+Kp} \tag{13.2}$$

where $V$ = volume of substance adsorbed at the pressure $p$

$V_m$ = the same in saturation, when $p \to \infty$, since the fractional coverage of a surface by the adsorbate is

$$\theta = \frac{V}{V_m} \tag{13.3}$$

The parameter $K$, having the meaning of the adsorption equilibrium constant, is related to the heat of adsorption by the equation

$$K = K_0 e^{Q_a/RT} \tag{13.4}$$

where $K_0$ = constant connected with the change in the entropy in adsorption

$Q_a$ = molar heat of adsorption (the subscript "a" will be omitted in the following for brevity).

Equation (13.2) can easily be checked experimentally, which is especially convenient to do if we rewrite it in the following form:

$$\frac{p}{V} = \frac{p}{V_m} + \frac{1}{KV_m} \tag{13.5}$$

Thus, if Eq. (13.5) is true, a linear relation should be obtained in the coordinates $p/V$ versus $p$. This relation makes it possible to calculate the parameters $V_m$ and $K$ from the tangent of the angle of inclination of the line and the section which it cuts off on the axis of ordinates. Experiments quite frequently give the required linear relation.

Surfaces are encountered, however, which this theory cannot be applied to. Let us consider, for example, the data on the adsorption of chlorine on silica gel at different temperatures shown in Fig. 13.1. It can be seen that there is no linear relation between $p/V$ and $p$, but within small pressure intervals linear sections of the isotherms can conditionally be separated. By extrapolation of each of these sections toward the axis of ordinates, we can see that the smaller the pressure, the smaller is the value of $1/KV_m$ for the given section of the isotherm and, therefore, the greater is the value of $K$ and correspondingly the greater is the heat of adsorption $Q$. For this reason the non-linear isotherms shown in Fig. 13.1 can be explained if it is considered that different sections of a surface have different adsorption potentials. At low pressures only centres with a high adsorption potential adsorb. As these centres become covered, with an increase in the pressure, the less active centres also gradually begin to participate in adsorption. The most proper way would probably be to draw curved isotherms in Fig. 13.1 and compute the parameters $V_m$ and $K$ for each pressure $p$ according to the position of the tangent to the curve at the given point. We would thus obtain a continuous relation between $Q$ and $p$ and a continuous distribution of the adsorption centres according to their adsorption potentials.

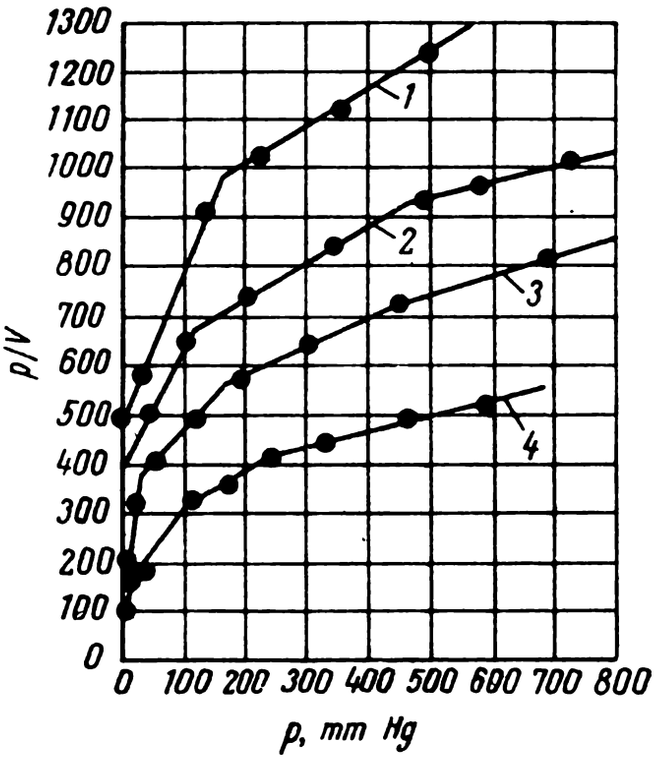



Fig. 13.1. Isotherms of adsorption of chlorine on silica gel:
1—at 88.5 °C; 2—at 66.5 °C; 3—at 51 °C; 4—at 35.9 °C

The adsorption heterogeneity of some surfaces can also be experimentally proved in a different way. Figure 13.2 shows data of H. S. Taylor on the heats of adsorption of ammonia on an iron catalyst obtained as follows. The ammonia was adsorbed on the catalyst in consecutive portions of two cubic centimetres, and each time the heat of adsorption was determined. It can be seen that as the surface

is covered, the heat of adsorption regularly decreases, i.e. less and less active sections of the surface are covered by the adsorbate. The stepped curve constructed on the basis of experimental data, with an increase in the number of experiments and a reduction in the volumes of the adsorbed ammonia (a greater number of points), in the limit would give the true distribution of the sections of the surface by heats of adsorption. This is shown by a dotted line in Fig. 13.2.

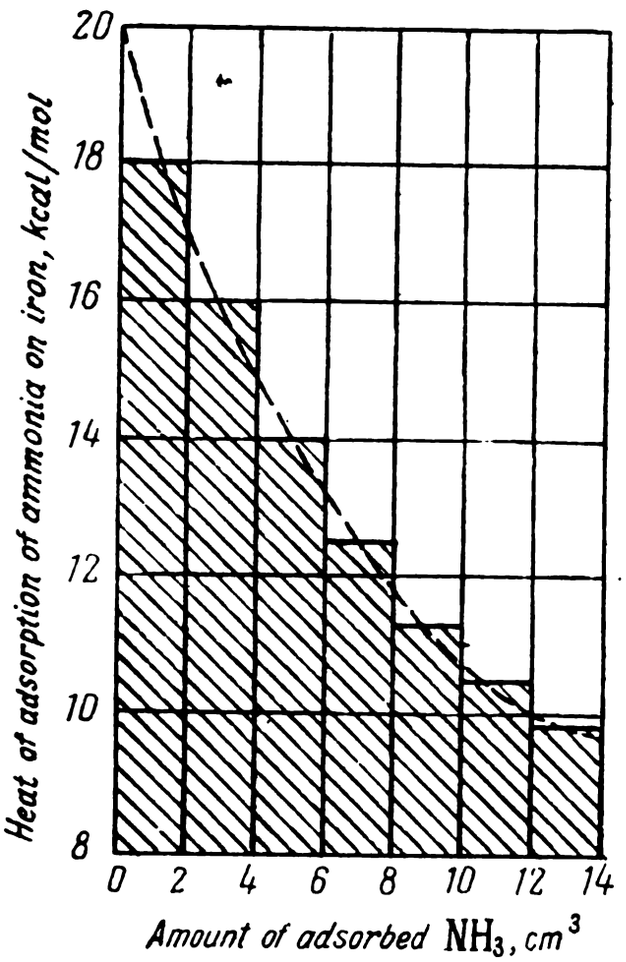



Fig. 13.2. Heat of adsorption of ammonia on iron catalyst

Let us also consider the *differential-isotope* method of detecting the heterogeneity of a surface developed recently (S. Roginsky and N. Keyer). The essence of this method consists in the following. A definite portion of a gas of one isotope composition is first adsorbed on the surface, and then a portion having another isotope composition. After this separate portions of the gas are desorbed and their isotope composition is analysed. If the surface being studied is homogeneous, the composition of the desorbed gas should be the average one of all the portions adsorbed at different times, since desorption should proceed uniformly from all the occupied centres of the surface. If the surface is heterogeneous, the sequence of desorption should be the reverse to that of adsorption. The composition of the first portions of the desorbed gas should coincide with that of the last adsorbed portions, since on a heterogeneous surface adsorption first proceeds on centres with a great adsorption potential, and only after their coverage does the adsorption ability of the less active centres manifest itself. Desorption, on the contrary, first takes place from the less active sections of a surface. This method made it possible to discover the adsorption heterogeneity of some surfaces[1] (metallic nickel, zinc oxide, carbon, etc.).

Thus, experiments show that the real surface of an adsorbent is heterogeneous and different parts of it have a different adsorption potential.

[1] It should be noted that the presence of heterogeneity and its nature, especially for adsorbents with a developed surface (various carbons and coals, silica gels, aluminogels, etc.) depend on how the samples are prepared.

2. *Poisoning of Catalysts.* Data on the action of poisons on heterogeneous catalysts show that the catalytic activity of different parts of the surface of catalysts is heterogeneous as a rule. Let us consider, for example, the data of R. Pease on the poisoning action of carbon monoxide on copper catalyzing the hydration of ethylene. The adsorption of 10 $cm^3$ of carbon monoxide corresponds to the adsorption saturation of the surface of 100 g of copper (i.e. $V_m = 10$ $cm^3$), but the adsorption of 0.05 $cm^3$ of CO already suppresses the initial catalytic activity of the copper by 90%. Consequently, 10 $cm^3$ of CO correspond to the total number of adsorption centres (or the entire surface), while 0.05 $cm^3$ of CO corresponds to 90% of catalytically active centres (or 90% of the catalytically active part of the surface). The amount of CO corresponding to the entire complex of catalytically active centres is $\frac{100 \times 0.05}{90} = 0.055$ $cm^3$, while the catalytically active centres form only $\frac{100 \times 0.05}{10} = 0.55\%$ of all the adsorption centres. Similar results were obtained for many other catalysts. Consequently, a surface consists of a complex of adsorption centres, of which only a small part are also catalytically active centres.

The fact that the adsorption of reacting molecules on a catalyst is as a rule activated adsorption indicates that the reaction of the adsorption centre with the substrate leads to the formation of a surface compound of the chemisorption type. Hence the following conclusion suggests itself: only such adsorption centres (or groupings of them) are catalytically active on which the adsorbate is capable of forming an intermediate that is active for conducting the given catalytic process. The development of this view leads to more specific establishment of the geometrical and energy nature of the active centres of catalysts.

3. *Taylor's Theory of Active Centres.* According to this theory (the 1920's), the surface atoms of a crystal lattice which for some reason or other are higher than the mean level of the surface are the active centres of a catalyst. Such crystal "peaks" have free valences and are capable of forming reactive intermediates. The idea of the active part of a surface as a formation which is anomalous in comparison with a normal crystal surface has been confirmed by a number of qualitative experiments. For example, W. Palmer and F. Constable, investigating the dehydration of alcohols on metallic copper, i.e.

$$R-CH_2-OH \xrightarrow{Cu} R-CH=O+H_2$$

studied the influence of the method of preparation of the catalyst on its activity. It was found that methods leading to the formation of a sufficiently "smooth" surface—electrolytic deposition, reduction of a solution of $[Cu(NH_3)_4]^{2+}$ with hydrazine hydrate, etc.—give

inactive specimens. Conversely, if the preparation (passing of ammonia over a copper screen at 820 °C, the rapid reduction of copper salts and CuO with carbon monoxide, thermal decomposition of the copper salts of monobasic fatty acids) causes imperfections in the crystal lattice, a catalytically active surface is obtained. Although Taylor's concept is a purely qualitative one, from the historical viewpoint it is an important step in the development of the theory of catalysis, since Taylor was the first to put forward the idea of the existence of an active centre and to characterize its structure.

4. *Relation between Parameters of the Arrhenius Equation.* Many investigators noticed that when the same process is conducted on different catalysts (of a different chemical nature or prepared in different ways), there is a relation between the parameters $C$ and $E$ in the Arrhenius equation $k = Ce^{-E/RT}$ that is described by the equation

$$C = ae^{E/h} \tag{13.6}$$

or in the logarithmic form

$$\ln C = \ln a + \frac{E}{h} \tag{13.7}$$

where $a$ and $h$ are constants.

This relation is quite surprising, since it would seem that there should be no relation between the quantities $C$ and $E$. The quantity $E$ is connected with the energy nature of an active centre, while $C$, with an accuracy to the factor of proportionality, is the number of active centres per unit of catalyst surface. To date no complete theoretical substantiation of this interesting experimental law has been given.[1] Most likely the explanation given by G. Schwab on the basis of the theory of active centres is the most verisimilar one. If catalysis is carried out only by definite active centres having a different energy potential (i.e. catalysis proceeds on a set of active centres with different activation energies on them), then from statistical thermodynamic considerations their number should grow with a reduction in the energy potential. On the surface of a catalyst which in accordance with the conditions of its preparation has centres with a high activity, it is only these centres that will participate in a process. On the surface of a catalyst having no centres with a high activity, the catalysis will be conducted by less active, but more numerous centres. Consequently, the greater the value of $E$ for a given catalyst from among a series of catalysts with a different activity of their centres, the higher is the value of $C$ that can be expected. Since an exponential relation is the most probable between the number of centres and their energies, empirical equation (13.6) can also be explained from a qualitative viewpoint.

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[1] It may be that in certain cases there is also a purely algebraic effect. The quantity $C$ is found by calculations from independently determined values of $k$ and $E$. In the conditions of an experiment the value of $k$ rarely changes more than within the limits of one order, and $\log k$ changes to a still smaller degree. Considering $\log k$ to be constant, we obtain approximately $\log C = \log k + \frac{E}{2.3RT} \approx$ $\approx \text{const} + \frac{E}{2.3RT}$. Therefore, a change in the experimental value of $E$ for different catalysts also leads to the obtaining of a change in the calculated value of $C$. With an increase in $E$ the value of $\log C$ will grow, and with a decrease in $E$ it will diminish.

5. *Theory of Supersaturation. "Sintering"*. If we assume that the active centres are sections of the surface parts of a lattice characterized by a deviation from the equilibrium state, then it will be natural to assume that a catalyst will be more active if the conditions of its preparation facilitate the forming of the greatest possible number of surface imperfections of the crystal lattice. Since an ideal crystal, all of whose particles are arranged at the lattice points[1], is the thermodynamically most stable form, it would seem that all the deviations of a crystal from the thermodynamically equilibrium state should lead to an increase in its catalytic activity. In this connection the thermodynamic aspect of the theory of active centres appears, namely, the *theory of supersaturation* proposed by S. Roginsky. According to this theory, all catalytically active systems have an increased Helmholtz energy $A_{sup}$ in comparison with the minimum Helmholtz energy $A_0$ of the thermodynamically equilibrium state, i.e. are *supersaturated*. A measure of supersaturation and, therefore, of the activity of a specimen is the excess of Helmholtz energy

$$\Delta A = A_{sup} - A_0 \quad (13.8)$$

Supersaturation may occur in the process of preparation of a catalyst. Its cause may be the presence of metastable phases, lattice imperfections, impurities, an increased dispersity and the like.

Figure 13.3 gives data on the kinetics of sintering (the dependence of the activity on the duration of initial heat treatment of the catalyst) of platinum black at 200, 350 and 450 °C (the activity was determined according to the decomposition of hydrogen peroxide). At a low temperature of preliminary calcination (200 °C) this relation has a complicated polyextremal nature, although it is reproduced for the given sample at separate points. The activity increases or decreases in comparison with the initial one depending on the duration of preliminary calcination, but on an average it remains quite high. It can be assumed that here there are indeed no equilibrium relations between the crystalline phase of the catalyst and the active centres on its surface, and that the system consecutively passes through metastable states. But at higher temperatures the nature of the relation is quite unambiguous. There is a rapid drop in the activity to a definite level corresponding to the given temperature, after which a further increase in the duration of preliminary calcination does not change the activity of the catalyst. Obviously, even if there is no true equilibrium here in a strictly thermodynamic sense, nevertheless a certain stationary state of the lattice is maintained with a definite number of active centres on its

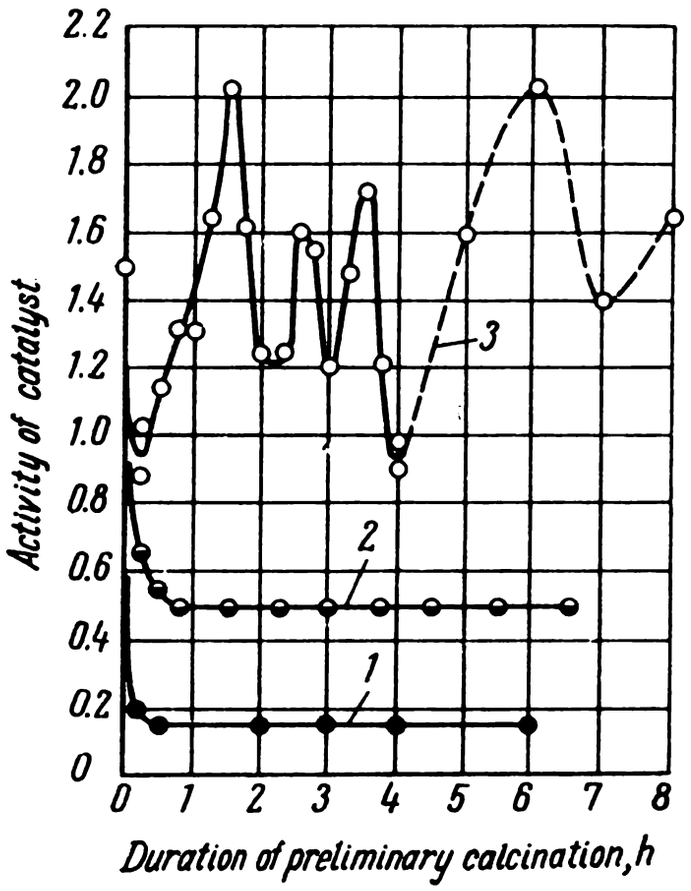



Fig. 13.3. Kinetics of sintering of platinum black:
*1*—at 450 °C; *2*—at 350 °C; *3*—at 200 °C

[1] Any ideal crystal at a temperature above absolute zero has a thermodynamically equilibrium number of crystal lattice imperfections both in the bulk and on the surface.

surface. The result is that a constant (at the given temperature) level of activity is maintained. It should be noted that in general the average level of the activity is the higher, the further the system is from such a stationary state, which qualitatively is in agreement with the theory of supersaturation.

The specific activity, depending on the temperature of preliminary calcination of the catalyst, frequently has a maximum. Figure 13.4 shows an example of such a relation for silver catalysts of the decomposition of formic acid. While the total surface area of the catalyst as a result of thermal growth of the crystals decreases regularly with an increase in the temperature of two-hour preliminary heating, the specific activity has a clearly seen maximum at about 600 °C. This means that with a growth in the temperature the number of active centres per unit of surface area first grows and then, beginning from a definite temperature, decreases. Such curves cannot be explained on the basis of our notion of sintering as surface "fusion" of the active centres or on the basis of the effect connected with a decrease in the total surface area upon an increase in the temperature. This phenomenon was considered from the standpoint of thermodynamics by O. Poltorak, who adopted the following model. The active centres are an "atomic phase" that is adsorbed on the surface of a crystal. It was found that for finely dispersed crystals the amount of "atomic phase" per unit of surface area decreases with a growth of the crystals. Thus two competing processes occur with a change in the temperature. Initially with an increase in the temperature the number of defects grows and, consequently, their surface concentration. With a further increase in the temperature, the growth in the number of defects and their mobility leads to a growth of the crystals and, therefore, to a reduction in the surface concentration of the defects.

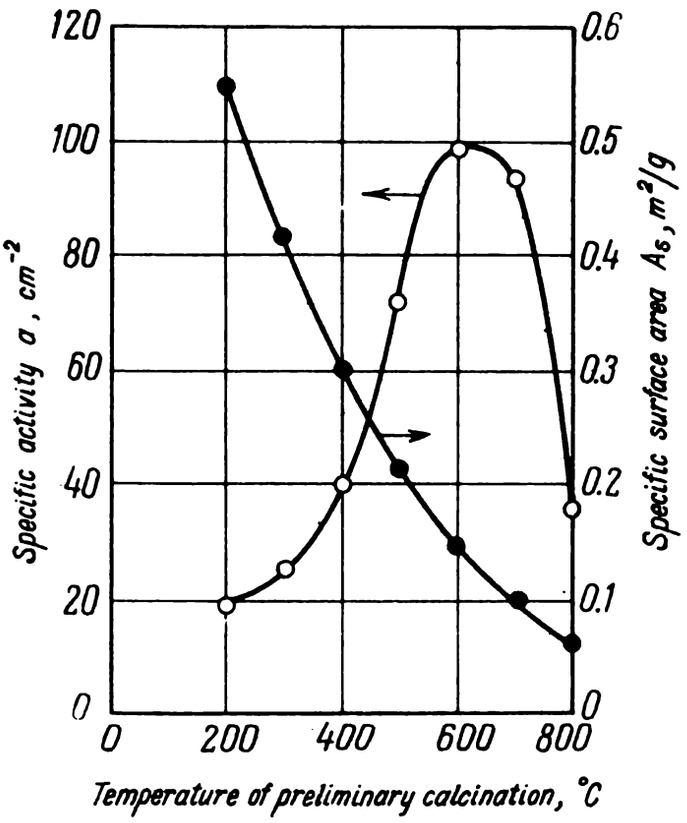



Fig. 13.4. Dependence of specific activity and specific surface area of silver catalyst on temperature of preliminary calcination

In addition, the theory of supersaturation does not give a specific model of an active surface. However, the idea that in the final run a catalyst is the more active, the more its state deviates from an equilibrium ideal one, can be useful for an experimenter preparing a catalyst.

Whatever the concrete views on the mechanism of catalysis, the existence of active centres on the surface of the catalyst is generally acknowledged. A different viewpoint also exists, however. For example, G. Boreskov considers that there are no active centres and that catalytic activity is a property of the entire surface of a solid. Hence it follows that the activity is directly proportional to the total surface area of the catalyst and depends only on its chemical composition. For this reason catalysts of the same chemical compo-

sition must have a constant specific activity. For certain metal catalysts such a viewpoint is confirmed by experimental data. As a whole, however, this idea contradicts an enormous amount of experimental material on the poisoning and sintering of catalysts (the established heterogeneity of the surface of many active systems and the lack of equality between the concepts of the adsorption and the catalytically active parts of a surface, data on the catalytic activity of catalysts on supports). It could not explain a considerable amount of experimental facts discovered in the studying of heterogeneous catalytic processes.

**13.2. Defects of Crystal Lattice and Model of Active Surface in Theories of Heterogeneous Catalysis.** If we consider an ideal crystal at absolute zero as a hypothetical initial model of a solid, all the atoms forming it will occupy quite definite sites, forming a regular crystal lattice. With an increase in the temperature, thermal motion of the atoms will violate this order. Some of the atoms may leave their places at the lattice points (vacant points are formed) and take up an interstitial position ("Frenkel defects"). In this way pairs of vacancies and interstitial atoms are created. Sometimes atoms may diffuse from the crystal interior to the surface. In this case only vacancies are formed in the lattice ("Schottky defects"). At a given temperature $T$ the number $n$ of defects of a given type in thermodynamic equilibrium with the crystalline phase is determined by the expression

$$n = n_0 e^{-U/RT} \tag{13.9}$$

where $U$ is the energy of formation of a defect of a given kind.

The formation of defects in the bulk naturally leads to their formation on the surface, the appearance on it of vacant sites and of atoms on the faces of the lattice at places not provided for by a regular crystal order. Since all these formations are in equilibrium with the lattice, a reduction of the temperature (a sufficiently slow one) leads to a decrease in their number, and at absolute zero the crystal returns to its initial state with regular arrangement of the atoms. Such defects are usually called thermal ones.

A real crystal differs from an ideal one in that as a result of the conditions of its genesis it has different imperfections of its lattice. These imperfections include *dislocation*, i.e. different distortions of the lattice planes in comparison with their geometrically regular arrangement in an ideal crystal. For example, one of the planes may be absent in part of the bulk of the crystal, which results in distortion of the interplane distances in this part of the crystal (*edge dislocation*). One or several planes may be distorted, which in the growth of a crystal sometimes leads to further distortion of the lattice (*screw dislocation*). The emergence of the dislocations onto the surface

results in the formation of irregular faces and edges with different geometrical imperfections. In addition, imperfections of a stoichiometric nature—deviation of the composition of the crystal from a simple empirical formula—may appear for various reasons in the formation of a crystal.

Violations of stoichiometry and also impurities inevitably lead to local geometrical distortions in a crystal. All these imperfections may sometimes result in a crystal being divided by "cracks" into separate microcrystalline blocks fastened to one another to a certain extent. Such a block structure is characteristic of many crystalline bodies having a great significance in heterogeneous catalysis. Thus a real crystal, in addition to thermal defects due to thermodynamic causes, contains irreversible defects connected with the history of formation of the given specimen, the so-called *biographical* defects. Since lattice imperfections lead to inequality between the separate elements of a crystal from an energy viewpoint, their presence facilitates the formation of an additional number of thermal defects, which may be much more numerous than in an ideal crystal. Deviations from the properties of an ideal crystal may be detected experimentally. Thus, dry crystals of table salt are destructed at tensions of the order of 4 kgf/cm$^2$, while theoretical calculations give a value of the order of 200 kgf/cm$^2$. If the experiment is conducted with a crystal immersed in a saturated solution of the salt, i.e. in conditions when "healing" of the microdefects is possible, the test load approaches the theoretical one. Investigation of the intensity of reflection of x-rays from a crystal (C. G. Darwin) showed that many crystalline bodies consist of a complex of microcrystals turned toward one another at various angles. It was established that for most crystalline bodies the linear dimension of the separate blocks is $10^{-6}$ to $10^{-5}$ cm. The same result was obtained in investigating Laue diffraction patterns of mechanically deformed crystals (A. Joffe). A bulk block structure naturally results in a block structure of the surface, which is indicated, for example, by the etch figures on the surface of crystals (E. Andrade).

All the phenomena listed above result in the fact that the number of defects in a real crystal considerably exceeds the relevant number for a hypothetic ideal crystal. The diverse imperfections of the surface sharply increase the adsorption-active surface area and, therefore, the number of adsorption and catalytic centres. Since a real crystal may have the most diverse lattice imperfections, the active centres may have a different adsorption potential, i.e. energy heterogeneity of the surface appears. This is why the real structure of an active surface is, as a rule, taken into account in the theories of heterogeneous catalysis. Let us consider three models.

1. A *homogeneous surface* is one on all of whose active centres adsorption proceeds with the same heat of adsorption, and catalytic

transformation proceeds with the same activation energy. Experiments show that such surfaces are comparatively rare and are the most probable for purely metal catalysts. This model underlies the theory of the kinetics of heterogeneous catalytic reactions considered above. It will also underlie such concepts in which heterogeneity is ignored, for example the multiplet theory (A. Balandin) or the notion on the constancy of the specific activity (G. Boreskov).

On a real surface, firstly, there are centres with a different energy potential, and, secondly, it is divided by cracks, various dislocations and other geometrical imperfections that exceed in length the distances between the lattice points. One of these types of heterogeneity may prevail on separate specimens, depending on their chemical nature or history of preparation.

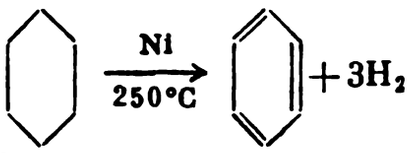
Let us consider two possible cases of the influence of these two factors on adsorption and catalysis.

2. *Heterogeneity of a surface* is expressed only in the energy nonequivalence of the active centres. A reactant getting onto such a surface is distributed among the adsorption centres in accordance with their energy and reacts in accordance with the activation energy on these centres. This model underlies the theory of adsorption and catalysis on heterogeneous surfaces (S. Roginsky, M. Temkin et al).

3. *Geometrical heterogeneity* and block division of the catalyst surface prevail. A reactant getting onto a block of the surface is adsorbed, and, if the given centre is also a catalytically active one, it reacts on the centres within the given block, regardless of the presence of centres "richer" in energy on other parts of the surface. It is obvious that here the decisive factor is no longer the energy distribution, but the distribution of the centres among the geometrical blocks—geometrical heterogeneity hides energy heterogeneity. The closest to such types of surfaces are polycrystalline bodies with a developed surface (alumina gels, silica gels, activated carbon, etc.). Such a model is used to explain the mechanism of formation of adsorption catalysts in the theory of active ensembles (N. Kobozev).

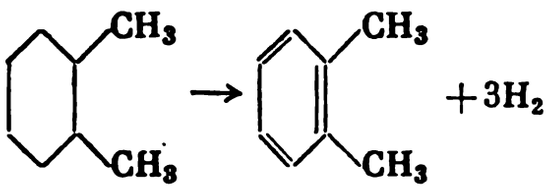
**13.3. Multiplet Theory of Catalysis.** The accumulated experimental data made it possible to define more specifically the concept *active centre* and compare its structure and composition either with the structure of molecules undergoing transformation (the multiplet theory) or with the nature of the process proceeding on a catalyst (the theory of ensembles). The structure of a molecule can determine to a considerable extent the nature of a catalytic transformation. For example, hydrocarbons with six-membered rings are quite easily dehydrogenated at a relatively low temperature on metallic nickel, asbestos applied to carbon, or platinum and palladium applied to alumina gel with the formation of the respective aromatic derivatives.

For example




cyclohexane benzene

It was found, however, that only hydrocarbons with a six-membered ring are capable of dehydrogenation, and only those which are capable of producing an aromatic ring. For example, of the two isomers of dimethylcyclohexane, dehydrogenation is possible for the 1-2-substituted compound, with the formation of xylene:




1,2-dimethyl-cyclohexane o-xylene

while 1,1-dimethylcyclohexane cannot be dehydrogenated on any of these catalysts. In condensed nuclei only six-membered rings dehydrogenate, while polymethylene rings having more than six carbon atoms isomerize in catalytic dehydrogenation forming a six-membered ring. For example, in the dehydrogenation of cycloheptane on platinum and palladium, methylcyclohexane is first formed, which then dehydrogenates to toluene.

These facts are explained by the structure of a molecule of the substance subjected to catalytic transformation. A different group of facts points to the influence of the structure of the catalyst on catalysis. Thus, it was found that metals having a definite crystallographic structure and interatomic distances in their lattice are catalysts of dehydrogenation.

A comparison of these two groups of facts and their explanation served as the initial foundation of Balandin's multiplet theory, which for the first time considers the composition of the active centre of a heterogeneous catalyst.

The basic tenets of this theory, first advanced in 1929, are as follows.

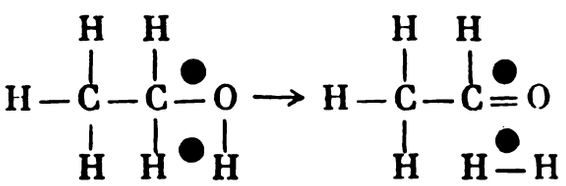
1. An active centre of a catalyst is a group of a definite number of adsorption centres arranged on a surface in geometrical accordance with the structure of the molecule undergoing transformation (the *principle of geometrical* or *structural similarity*).

2. In adsorption, a multiplet complex is formed on an active centre as a result of which redistribution of the bonds occurs that leads to the formation of the products.

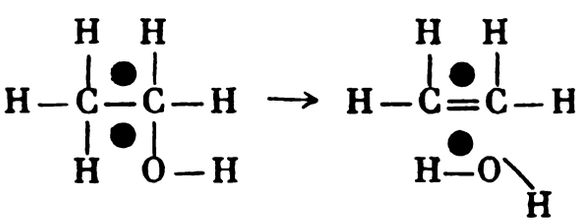
The multiplet theory places the geometrical arrangement of the adsorption centres in the active centre in a direct relation to the

geometrical structure of the molecules being catalyzed. This theory could be called the *theory of geometrical similarity of an active centre and a reacting molecule*. For various reactions the number of adsorption centres (each of which is identified with one atom of the metal) in an active centre is taken equal to 2, 3, 4, 6, etc. Such active centres were called *duplets*, *triplets*, *quadruplets*, *sextets*, and in the general case *multiplets*.

For example, dehydrogenation of ethyl alcohol according to the theory of multiplets occurs on a duplet, one atom of the duplet attracting hydrogen atoms of the groups $CH_2$ and OH, and the other atom—the oxygen atom and the carbon atom of the group $CH_2$. As a result the bonds C—H and O—H break, and the bonds H—H and C=O appear with the formation of molecules of acetic aldehyde and hydrogen (the atoms of the duplet on the surface of the catalyst are depicted by black circles):



If the distances between the atoms of the catalyst in the duplet will be different, another process is possible, namely, the hydrogen atom of the group $CH_3$ and the oxygen atom are attracted to one atom of the duplet, and both carbon atoms to the other one. The products of the reaction will be ethylene and water:



Other reactions require differe multiplets on the active centres. Thus, the dehydration of diethy her

$$C_2H_5OC_2H_5 \rightleftharpoons {}_2H_4 + H_2O$$

proceeds on a triplet, and the catalytic decomposition of ethyl acetate

$$2CH_3COOC_2H_5 \rightleftharpoons CH_3COCH_3 + C_2H_4 + C_2H_5OH + CO_2$$

on a quadruplet.

The most interesting results are obtained when the principle of geometrical similarity is applied to dehydrogenation of cycloparaffins. Good dehydrogenation catalysts are metals crystallizing in face-centered and hexagonal lattices, since only on the octahedral faces of the former and on the base pinacoids of the latter is an arrangement of the lattice atoms encountered that corresponds to the structure of six-membered rings. Only those metals are catalysts, however, in which the distance between the atoms in the lattice is within

the limits from $2.77 \times 10^{-8}$ cm (Pt) to $2.48 \times 10^{-8}$ cm (Ni). Thus, the face-centered lattices of Pd ($2.74 \times 10^{-8}$ cm), Ir ($2.70 \times 10^{-8}$ cm), Rh ($2.68 \times 10^{-8}$ cm), Cu ($2.56 \times 10^{-8}$ cm) are catalytically active, while the lattices of Th ($3.60 \times 10^{-8}$ cm), Pb ($3.50 \times 10^{-8}$ cm), Au and Ag ($2.88 \times 10^{-8}$ cm) having a crystallographically similar structure are not active catalytically in dehydrogenation of six-membered rings.

This is explained by the fact that geometrical similarity between the active centre and a molecule must be observed. The circumstance

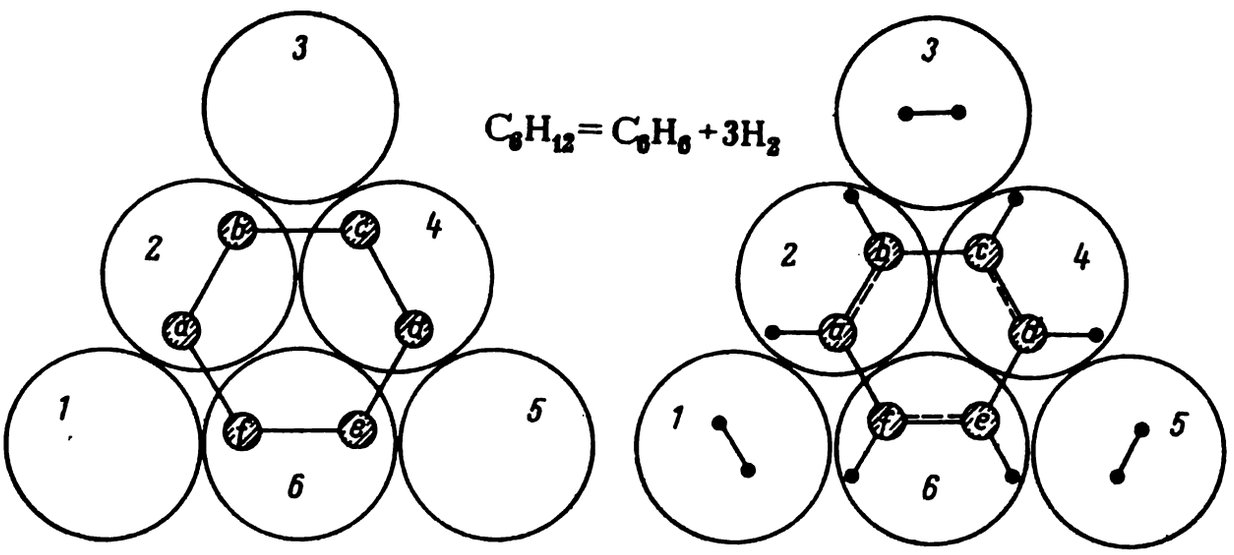



Fig. 13.5. Diagram showing dehydrogenation of cyclohexanes on a platinum sextet

that metals having definite parameters of their lattice are active shows that a slight deformation of the valence angles is possible in a multiplet complex within certain limits.

The arrangement of the atoms in a multiplet complex in the dehydrogenation of cyclohexane on a sextet is shown in Fig. 13.5 (here only the C—C bonds are shown in the molecule of cyclohexane). Atoms *1*, *3* and *5* of the catalyst pull the hydrogen atoms away from the carbon atoms *f*, *a*; *b*, *c*; and *d*, *e* respectively, and as a result of redistribution of the bonds hydrogen molecules are formed. Under the action of the catalyst atoms *2*, *4* and *6* double bonds are formed between the carbon atoms *a* and *b*, *c* and *d*, *e* and *f*. The products are three molecules of hydrogen and a molecule of benzene.

The above example shows that the multiplet theory considers an active centre as a definite part of the surface of a normal crystal lattice. Proposing various active centre models, for example the sextet model of dehydrogenation of a six-membered ring, the multiplet theory makes it possible to qualitatively explain the empirical laws found in studying the catalytic transformations of many organic substances.

Deviations from the simple scheme of geometrical similarity of the multiplet theory were also obtained in a number of subsequent investigations. Thus, it was found that an active centre in the dehydrogenation of cyclohexane on $Cr_2O_3$ has two, and not six atoms. In this connection it became necessary to make the assumption that a cyclic molecule adsorbed by its rib consecutively rotates on the duplet[1]. In appropriate conditions five-membered rings can also be dehydrogenated on the same catalyst $Cr_2O_3$.

These anomalies show that the true mechanism of catalysis is more complicated and diverse than the simple scheme of the multiplet theory. This does not reduce the significance of the theory, however, since for the first time it has seriously raised the question of the structure and composition of an active centre of a heterogeneous catalyst.

A second tenet of the multiplet theory is the principle of energy similarity (1935), according to which the activation energy of a heterogeneous reaction is a complex quantity consisting in the first approximation of two addends, one of which depends only on the energy of the bond between the composite parts of the reacting molecules, and the other on the energy of interaction between a catalyst and the composite parts of a multiplet complex. The question of the dependence of the activity of a catalyst on its affinity to the reacting parts of a system also follows from the principle of energy similarity. According to this principle, a heterogeneous catalytic reaction can be represented by the following scheme:

$$\text{Reactants} + \text{Catalyst} \longrightarrow \text{Multiplet complex} \longrightarrow \text{Catalyst} + \text{Products}$$

To carry out the first step (the formation of a multiplet complex), the reacting molecules must have the energy required for breaking the bonds, the energy of formation of the multiplet complex being liberated. The activation energy is the difference between these energies (in the first approximation). It should obviously decrease with an increase in the affinity of the catalyst to the substrate. To carry out the second step (decomposition of the multiplet complex with the formation of the products), an energy must be imparted to the multiplet complex that is required for breaking the bonds in it. As a result the energy of formation of the products is liberated. The difference between these energies determines the rate of the second step. Thus, an unlimited increase in the affinity of a catalyst to its substrate does not lead to an unlimited acceleration of the catalytic process. Up to a certain limit (as long as the rate of the process is determined by the first step) the activation energy will

[1] This assumption is difficult to substantiate from the thermodynamic viewpoint, since the adsorption affinity of a double bond to a catalyst is in the general case greater than the adsorption affinity of a single bond.

decrease and the activity of the catalyst will grow. With a further increase in the bond energy in the multiplet complex, however, the rate of the process will be determined by the second step, and the activation energy (second step) will grow. For this reason a further increase of the affinity in the multiplet complex will retard the process.

**13.4*. Adsorption and Catalysis on Heterogeneous Surfaces.** The theory of the kinetics of heterogeneous processes is based on the application of the Langmuir adsorption equation, which was derived on the assumption that a surface is homogeneous and that there is no interaction between the adsorbed molecules. The first of these assumptions is equivalent to the fact that the heat of adsorption $Q$ has the same constant value on all the adsorption centres. For catalytically homogeneous surfaces, the constancy of the activation energy for all the active centres of the catalyst must additionally be observed. If these conditions are not observed, and the heat of adsorption changes for different centres within broad limits from $Q_{min}$ to $Q_{max}$ (or the activation energy changes from $E_{min}$ to $E_{max}$), the surface is called a heterogeneous one, and, obviously, to describe the processes proceeding on it, it is necessary to introduce definite corrections into the expressions deduced for homogeneous surfaces.

Let us first of all consider adsorption on a heterogeneous surface. As indicated previously, in the Langmuir equation $\theta=\frac{Kp}{1+Kp}$ the coefficient $K$ is the constant of equilibrium between the gaseous phase and the surface and can be expressed through the thermodynamic parameters of adsorption:

$$K=\frac{\theta}{p(1-\theta)}=e^{\Delta S_a/R}e^{-\Delta H_a/RT}=K_0e^{Q/RT} \tag{13.10}$$

where $Q=-\Delta H_a$ = heat of adsorption
$K_0$ = coefficient related to the entropy of adsorption $\Delta S_a$.

Let us assume that for regions with an identical heat of adsorption the Langmuir equation is obeyed with the given value $Q_i$:

$$\theta=\frac{K_0e^{Q_i/RT}p}{1+K_0e^{Q_i/RT}p} \tag{13.11}$$

To obtain an equation for the entire surface, it is necessary to know the distribution function $f(Q)$ of the adsorption centres by values of $Q$. At a certain value of the heat of adsorption $Q$ this function will give the fraction of the centres on which the heats of adsorption are within the limits from $Q$ to $Q+dQ$. By definition, $f(Q)$ should be rated, i.e. an integral taken over the entire surface should be equal to unity:

$$\int_{(A)} f(Q)\,dQ=1 \tag{13.12}$$

Hence for the entire surface the fractional coverage at the given value of $p$ will be

$$\theta=\frac{\int_{Q_{min}}^{Q_{max}}\theta f(Q)\,dQ}{\int_{Q_{min}}^{Q_{max}}f(Q)\,dQ}=\int_{Q_{min}}^{Q_{max}}\theta f(Q)\,dQ=\int_{Q_{min}}^{Q_{max}}\frac{K_0e^{Q/RT}p}{1+K_0e^{Q/RT}p}f(Q)\,dQ \tag{13.13}$$

At $T$ = const Eq. (13.13) is one of an adsorption isotherm, and at $p$ = const of an adsorption isobar for a heterogeneous surface. To solve this equation we must know the analytical form of the function $f(Q)$. Let us consider a simple example when $f(Q)$ is constant, i.e. the number of adsorption centres is uniformly distributed among all the values of $Q$:

$$f(Q) = B \tag{13.14}$$

where B is a constant. The isotherm equation will now become

$$\theta = BK_0pRT \int_{Q_{min}}^{Q_{max}} \frac{e^{Q/RT}}{1+K_0pe^{Q/RT}} d\left(\frac{Q}{RT}\right) =$$

$$= BRT \ln \frac{1+K_0e^{Q_{max}/RT}p}{1+K_0e^{Q_{min}/RT}p} = BRT \ln \frac{1+K_{max}p}{1+K_{min}p} \tag{13.15}$$

The first portions will be adsorbed on centres with the greatest heat of adsorption, and only when they are covered will adsorption proceed on the parts of the surface with a smaller and smaller heat of adsorption. Therefore for the average coverage of the surface by the adsorbate the inequalities $K_{max}p \gg 1$ and $K_{min}p \ll 1$ are observed, whence we obtain an approximate form of the equation

$$\theta = BRT \ln K_{max}p \tag{13.16}$$

Thus a logarithmic isotherm experimentally obtained by A. Frumkin and A. Shlygin and theoretically deduced for the first time by M. Temkin corresponds to uniform distribution.

With some analytical forms of the relation $f(Q)$ the integral (13.13) either cannot be taken in a finite form in elementary functions, or, if it can, the expressions obtained are quite cumbersome and inconvenient for practical use. This is why methods of approximate solution of equations of type (13.13) play an important part in the theory of processes on heterogeneous surfaces. Let us consider the method of approximation developed in the investigations of S. Roginsky.

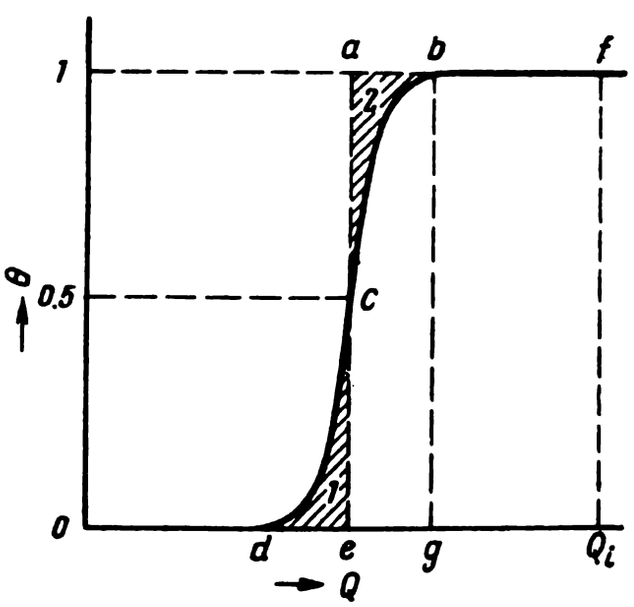



Fig. 13.6. Dependence of θ on $Q$

Let us plot the dependence of θ on $Q$ (Fig. 13.6). Since

$$\frac{\partial^2\theta}{\partial Q^2} = \frac{K_0pe^{Q/RT}}{(RT)^2(1+K_0pe^{Q/RT})^3}(1-K_0pe^{-Q/RT}) \tag{13.17}$$

the abscissa of the point of inflection of the curve θ versus $Q$ will be

$$Q_c = -RT \ln K_0p \tag{13.18}$$

and the ordinate

$$\theta_c = 0.5 \tag{13.19}$$

It is assumed that with a sufficiently great heterogeneity the difference between areas *1* and *2* in Fig. 13.6 may be neglected, i.e. that the area limited by the cur-

ve $\theta = f(Q)$ is approximately equal to the area limited by the ordinate from the point of inflection and the straight line $\theta = 1$.

Figure 13.7 shows the process of adsorption in the coordinates $f(Q)$ and $Q$. At a certain value of $p$ the centres with a heat of adsorption from $Q_{max}$ to $Q'$ are covered, and the fraction of the surface covered is shown by the cross-hatched area. With an increase of the pressure the coverage grows and includes sections with a smaller $Q$. The fraction of the surface covered is always expressed by the

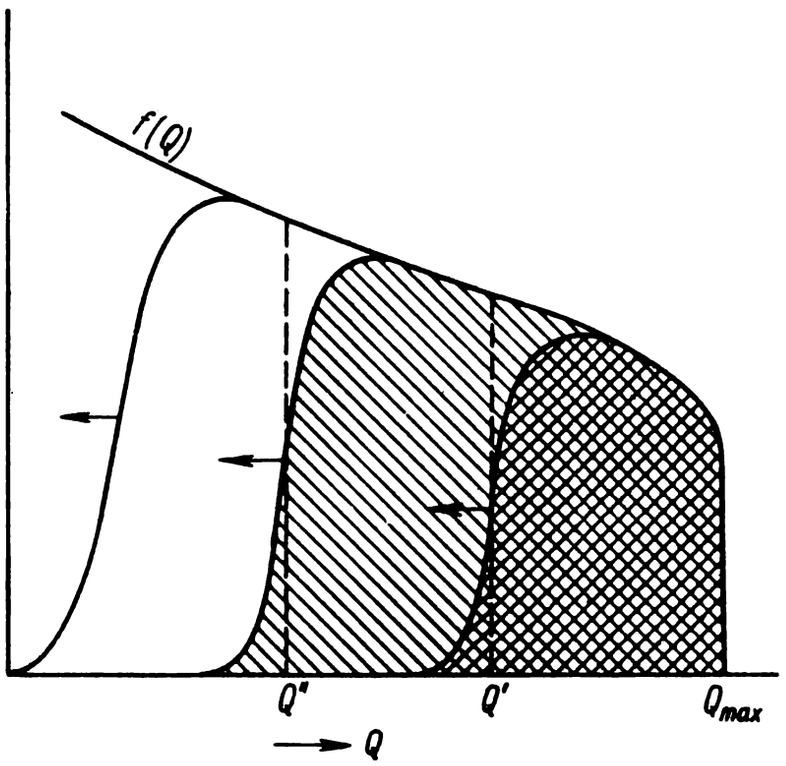



Fig. 13.7. Graphical representation of adsorption process

area confined by the curves of $\theta$ and $f(Q)$, but the approximation made allows us to replace the quantity $\theta$ by the ordinate of the point of inflection, and integral (13.15) by the simpler expression

$$\theta \approx \int_{Q_c=-RT \ln K_0 p}^{Q_{max}} f(Q)\, dQ \tag{13.20}$$

Using the method described above, let us derive an isotherm for the exponential distribution

$$f(Q) = \alpha e^{-mQ} \tag{13.21}$$

where $\alpha$ and $m$ are constants.

Hence

$$\theta = \alpha \int_{Q}^{Q_{max}} e^{-mQ}\, dQ = \frac{\alpha}{m}\left(e^{-mQ} - e^{-mQ_{max}}\right) \tag{13.22}$$

Since $Q = -RT \ln K_0 p$ and $Q_{max} = -RT \ln K_0 p_{min}$, this equation becomes

$$\theta = \frac{\alpha}{m}\left(e^{mRT \ln K_0 p} - e^{mRT \ln K_0 p_{min}}\right) = \frac{\alpha}{m}\left[(K_0 p)^{mRT} - (K_0 p_{min})^{mRT}\right] \tag{13.23}$$

At $p_{min} \ll p$ (i.e. at $Q_{max} \gg Q$) this equation can be simplified and written in a form corresponding to the Freundlich isotherm, namely:

$$\theta \approx ap^{1/n} \tag{13.24}$$

where $a = \frac{\alpha}{m} K_0^{mRT}$ and $\frac{1}{n} = mRT$.

This method can also be used to deduce isotherms and isobars for other kinds of the relation $f(Q)$. In addition, it was found possible to solve the reverse problem—find the distribution function according to the analytical form of an isotherm known from experiments.

Catalytic processes proceeding on a surface that is heterogeneous with respect to the activation energies can be considered in a similar way. It is necessary, correspondingly, to know the distribution function for the active centres by the reaction activation energies $f(E)$. Figure 13.8 shows the distribution function $f(E)$. It is sometimes more illustrative to express the distribution function through the rate constant of the catalytic process $k(E)$, which also depends on the activation energy:

$$k(E) = k_0 e^{-E/RT} \tag{13.25}$$

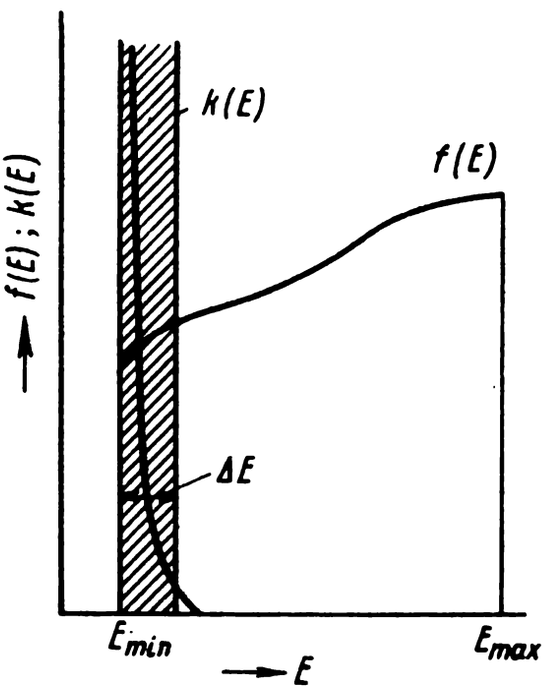



Fig. 13.8. Distribution function for surface heterogeneous with respect to activation energy

Such a relation is also shown in Fig. 13.8. Since $k(E)$ has the maximum value at $E_{min}$ and exponentially decreases with an increase in $E$, the process actually proceeds on a small fraction of the active centres having the smallest activation energies (naturally, if during the reaction there are no changes in the surface, for example self-poisoning of the active centres by the products). A definite section with a width of $\Delta E$ appears on the chart. It adjoins the edge of the distribution with the smallest values of $E$ and was called the *controlling band* by S. Roginsky. It is this band that determines the course of the entire process proceeding on the most active centres. If we cause the most active centres to fail in some way, for example poison them with a contact poison, the controlling band will shift to the right and the process on the same catalyst will proceed with a greater activaton energy.

**13.5. Catalysts on Supports. Adsorption Catalysts.** Only the surface of a solid metal catalyst is active, and it contains an insignificant part of all the molecules of the substance. To remedy this defects, catalysts on supports (carriers) were introduced quite a long time ago. These are catalysts in which the active substance (usually a catalytically acting metal) is applied to the surface of a solid that is catalytically inactive, but has a sufficiently developed surface. Customarily porous bodies such as silica gel, activated carbon, alumina gel, asbestos and pumice are used as the supports.

The most widespread way of preparing such catalysts is to apply a compound of the catalytically active metal onto the surface of the

support, with the following reduction or thermal decomposition of the metal. This results in a sharp growth oi the specific activity of the metal and its economy, which is especially important when such expensive metals as platinum, palladium, osmium and iridium are the catalysts. The support is not only capable of changing the activity of a catalyst within small limits. It is also a promoter, and sometimes affects the selectivity of the catalysts (M. Adadurov) and their thermal stability.

Thermal stability of a supported catalyst, as a rule, sharply increases in comparison with that of solid and powdered metal catalysts. For example, a drop in the activity of platinum black (in the decomposition of hydrogen peroxide) is already observed when it is heated to 300-350 °C. Platinum applied on silica gel does not practically change its activity when heated to 700 and even to 900 °C. By preventing sintering, the support prolongs the service life of the catalyst and increases the temperature range within which the catalyst is sufficiently active. As a result it is often possible to raise the temperature of conducting a reaction, thus accelerating it and increasing the yield of useful products.

Just as striking is the resistance of supported catalysts to poisons. For example, crystalline palladium upon the adsorption of $2.5 \times \times 10^{-4}$ gramme-atom of poison (mercury ions) per gramme-atom of palladium loses 86.9% of its catalytic activity. Palladium adsorbed on activated carbon with the same proportion of the poison and active metal loses only 17% of its initial activity. Similar results are observed for other catalysts.

These effects can be explained on the basis of the block structure of the support surface. Surface defects limit the surface mobility of the applied atoms, which are localized in the surface blocks—*regions of free migration* (according to N. Kobozev). The result is that an increase in the temperature leads to the formation on the support surface of geometrical and energy barriers. The latter prevent thermal motion along the surface and do not allow the active component to "sinter" into an inactive or only slightly active complex of atoms, as would occur on an ideal crystal surface. The molecules of the poison are adsorbed not only on the active centres of the catalyst, but also on the adsorption centres of the support. In addition, a considerable portion of them is localized in the regions of migration, which for some reason are deprived of active centres.

An important characteristic of a supported catalyst is the concentration of the catalyst atoms on the surface of the support, i.e. the number of atoms per unit of support surface area. It is the most convenient to express this concentration through the fractional (surface) coverage $\theta_c$, determined by the relation

$$\theta_c = \frac{A_{Me}N}{A_s} \tag{13.26}$$

where $A_s$ = surface area of 1 gramme of the support (specific area)
$A_{Me}$ = surface area occupied by a catalyst atom
$N$ = number of catalyst atoms applied to 1 gramme of the support.

Thus the fractional coverage is the fraction of the surface occupied by atoms of the catalyst.

Catalysts on a support have not only a purely practical significance. By preparing greatly diluted, so-called adsorption catalysts, it is possible to produce active specimens for which the fractional coverage of the support by the active substance is equal to $10^{-2}$-$10^{-4}$ of a monoatomic layer. Owing to the block structure of the surface, its mobility in such specimens is completely limited by the regions of migration, and practically all of the applied substance is in the adsorbed precrystalline state. In this connection the problem appears of determining the distribution of the total number of $N$ atoms applied to the surface by regions of migration, i.e. to determine the number of migration regions that will be covered with a certain number of catalyst atoms.

Let us consider how catalyst atoms will be distributed on the surface of a support constructed of a complex of fine crystalline blocks. To simplify our reasoning, we shall assume that the applied atoms do not react with one another. We thus obviously limit the concentration of the layer, which as a minimum should be from one-tenth to one-hundredth of the concentration of a monoatomic layer. In addition, let us take the mean value of the migration region $\Delta$, whence

$$Z_0 = \frac{A_s}{\Delta} \tag{13.27}$$

where $Z_0$ is the number of migration regions on the surface of one gramme of the support.

On the basis of the equal probability of the catalyst getting into a certain region of migration, let us find the probability of formation of an $n$-atomic ensemble of catalyst atoms in one region. If $N$ catalyst atoms are applied to the surface of one gramme of a support, then the average number per region will be

$$\nu = \frac{N}{Z_0} \tag{13.28}$$

The probability of one of the total number $N$ of atoms getting into the given migration region is $1/Z_0$ (on condition that their surface areas and accessibilities are assumed to be the same), and the probability of $n$ atoms getting into this region is $(1/Z_0)^n$.

It should be taken into account, however, that the remaining $N - n$ atoms will get into any of $Z_0 - 1$ regions except for the selected one. The probability $P_0$ of the formation of an $n$-atomic

ensemble of catalyst atoms will be

$$P_0 = \left(\frac{1}{Z_0}\right)^n \left(\frac{Z_0 - 1}{Z_0}\right)^{N-n} \tag{13.29}$$

Since the places of all the atoms can be changed without changing the distribution being sought, we can obtain the total probability

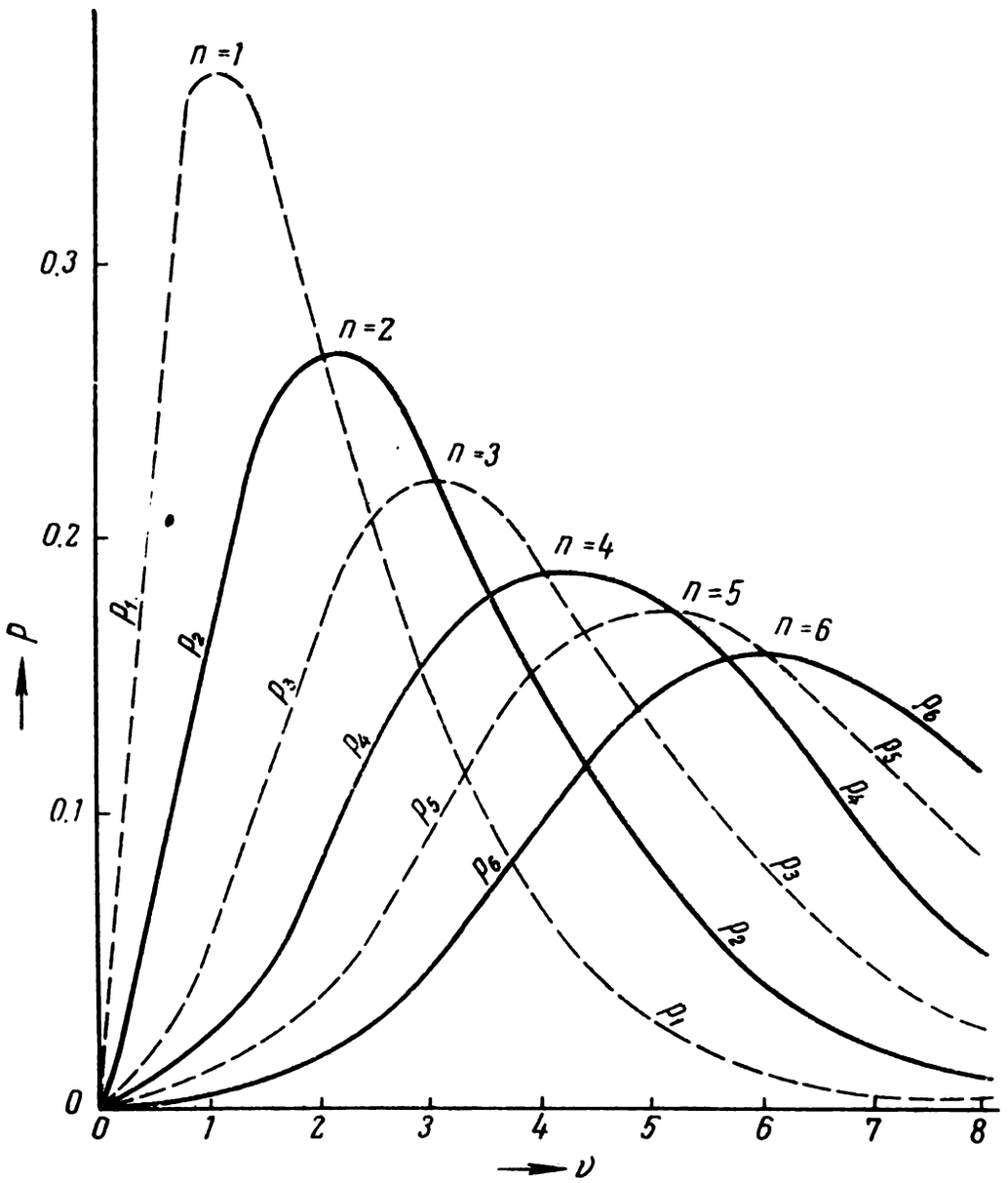



Fig. 13.9. Dependence of probability $P$ of formation of atomic ensembles on the average number of atoms $\nu = N/Z_0$ in a migration region

$P$ of the formation of an $n$-atomic ensemble in one migration region by multiplying Eq. (13.29) by the number of combinations of $N$ taken $n$ at a time:

$$P = \frac{N!}{n!(N-n)!}\left(\frac{1}{Z_0}\right)^n \left(1 - \frac{1}{Z_0}\right)^{N-n} =$$

$$= \frac{N!}{n!(N-n)!}\left(\frac{\nu}{N}\right)^n \left(1 - \frac{\nu}{N}\right)^{N-n} \tag{13.30}$$

Seeing that $N \gg n$, the limit transition is justified:

$$P_n = \lim_{N \to \infty} P = \frac{\nu^n}{n!} e^{-\nu} = \frac{(N/Z_0)^n}{n!} e^{-N/Z_0} \tag{13.31}$$

Thus, on the basis of the assumed model, we get the distribution of the catalyst atoms described by Poisson's law, which is applied in many fields of physics, for example in the theory of fluctuations.

Equation (13.31) shows that a definite number of ensembles of a certain composition corresponds to each value of $N$. Figure 13.9 shows the curves $P_n = f\left(\frac{N}{Z_0}\right)$. It can be seen that each curve has a maximum at $n = \nu = \frac{N}{Z_0}$.

Since the absolute number of catalyst atoms on a surface is known for adsorption catalysts, we can introduce the absolute value of the catalytic activity, which will allow us to compare the efficiency of various catalysts (see Chap. 12). We shall define the total catalytic activity $A$ as the number of substrate molecules reacting per second on all the catalyst atoms on the surface of one gramme of a specimen, i.e.

$$[A] = \text{molecule/s} \cdot \text{g} \tag{13.32}$$

The specific activity $a = A/N$ is the number of molecules reacting per second on one atom of the catalyst, i.e.

$$[a] = \text{molecule/s} \cdot \text{atom} \tag{13.33}$$

**13.6. Theory of Active Ensembles.** If any combinations of catalyst atoms that get onto the surface of a support and remain attached to it are active catalytically, it is obvious that the total catalytic activity $A$ should be directly proportional to the number of applied atoms $N$ (at least until with a growth of $N$ part of the catalyst atoms begin to become lost as a result of partial crystallization), while the specific activity $a = A/N$ should remain constant.

If only definite combinations of atoms are active catalytically, for example $n$-atomic ensembles, the catalytic activity will be proportional to $P_n$ and will have a maximum depending on the value of $N$.

A selection between these two assumptions can be made only when experimental data are available. A great number of investigations were devoted to studying the dependence of catalytic activity on the concentration of the catalyst on the surface of the support. They showed that in the majority of cases the curves $A = f(N)$ have a maximum, and the curves $a = f(N)$ either have a maximum corresponding to a smaller amount of catalyst on the support, or exponentially drop with a growth of $N$. Experiments thus confirmed

the selective nature of the composition of an active centre for a definite process. Hence the problem appears of providing a method that would make it possible to determine the composition of an active centre for a definite process on the basis of the law of distribution of the catalyst atoms along the block surface of the support [Eq. (13.31)].

This problem was solved by N. Kobozev in 1939 in his theory of active ensembles. The basic tenet of this theory is as follows: the carrier of catalytic activity is the atomic (precrystalline) phase of the catalyst, relative to which the surface of the support (or the crystalline phase of the catalyst itself) performs the function of an inert substrate. For each given process an ensemble consisting of a definite number $n$ of catalyst atoms is the active centre.

If $N$ atoms of the catalyst are on the surface of one gramme of the support, then with $Z_0$ migration regions the number of $n$-atomic ensembles $Z_n$, with account taken of Eq. (13.31), will be

$$Z_n = Z_0 P_n = Z_0 \frac{\left(\frac{N}{Z_0}\right)^n}{n!} e^{-N/Z_0} \tag{13.34}$$

Denoting by $r_n$ the activity of one $n$-atomic ensemble, we can easily find an expression for the total $A_n$ and specific $a_n$ catalytic activities of an $n$-atomic ensemble:

$$A_n = r_n Z_n = r_n Z_0 \frac{1}{n!} \left(\frac{N}{Z_0}\right)^n e^{-N/Z_0} \tag{13.35}$$

$$a_n = \frac{A_n}{N} = r_n \frac{1}{n!} \left(\frac{N}{Z_0}\right)^{n-1} e^{-N/Z_0} \tag{13.36}$$

Both these expressions give a maximum with respect to $N$. Indeed

$$\frac{\partial A_n}{\partial N} = r_n \left(\frac{N}{Z_0}\right)^{n-1} \frac{1}{n!} e^{-N/Z_0} \left(n - \frac{N}{Z_0}\right) \tag{13.37}$$

whence

$$n = \frac{N^A_{\max}}{Z_0} \tag{13.38}$$

$$\frac{\partial a_n}{\partial N} = r_n \frac{1}{n} \frac{N^{n-2}}{Z^{n-1}} e^{-N/Z_0} \left(n - 1 - \frac{N}{Z_0}\right) \tag{13.39}$$

$$n - 1 = \frac{N^a_{\max}}{Z_0} \tag{13.40}$$

Solving the simultaneous equations (13.38) and (13.40) with the two unknowns $n$ and $Z_0$, we get the conditions that allow us to determine the number $n$ of atoms in an active centre and the number $Z_0$ of migration regions on the surface of a support from experimental

data:

$$n = \frac{N^A_{max}}{N^A_{max} - N^a_{max}} \tag{13.41}$$

and

$$Z_0 = N^A_{max} - N^a_{max} \tag{13.42}$$

Thus, by determining from experiments the position of the maxima on the curves of the total and specific activities ($N^A_{max}$ and $N^a_{max}$), it is easy to determine $n$ and $Z$, and then to find $r_n$ by Eq. (13.38) or (13.36).

It should be noted that any quantity proportional to $N$ can be used instead of it in Eqs. (13.38) and (13.39) and, consequently, in Eqs. (13.41) and (13.42). For example, if the surface area of a support $A_s$ is known, we can use the fractional coverage $\theta_c$ of this surface with atoms of the catalyst. Hence, on the basis of Eqs. (13.26) and (13.27) we get

$$\frac{N}{Z_0} = \frac{\Delta}{A_{Me}} \theta_c = s\theta_c \tag{13.43}$$

where

$$s = \frac{\Delta}{A_{Me}} \tag{13.44}$$

This quantity is the area of migration expressed through the number of atoms of the catalyst. Inserting Eqs. (13.43) and (13.27) into Eq. (13.35) and Eq. (13.43) into Eq. (13.36), we get

$$A_n = r_n \frac{A_s}{\Delta} \frac{(s\theta_c)^n}{n!} e^{-s\theta_c} \tag{13.45}$$

and

$$a_n = \frac{A_n}{N} = r_n \frac{A_s}{\Delta} \frac{(s\theta_c)^{n-1}}{n!} e^{-s\theta_c} \tag{13.46}$$

where the specific activity $a_n$ is related to a monoatomic layer of the catalyst on the surface of the support. To determine the parameters $n$ and $s$ according to Eqs. (13.41) and (13.42) we have

$$n = \frac{\theta^A_{c,\,max}}{\theta^A_{c,\,max} - \theta^a_{c,\,max}} \tag{13.47}$$

and

$$s = \frac{1}{\theta^A_{c,\,max} - \theta^a_{c,\,max}} \tag{13.48}$$

If $n = 1$, Eq. (13.36) becomes

$$a_1 = r_1 e^{-N/Z_0} \tag{13.49}$$

i.e. if the experimental curve of the specific activity has no maximum and exponentially drops with an increase in the concentration of the catalyst, a monoatomic ensemble is the active centre.

Let us consider an example of calculations according to experimental data. Figure 13.10 shows curves of the total and specific activities obtained in synthesizing ammonia on iron supported on alumina gel:

$$3H_2 + N_2 \xrightarrow{Fe/Al_2O_3} 2NH_3$$

From experimental data we have $N^A_{max} = 8.8 \times 10^{18}$ and $N^a_{max} = 6.1 \times 10^{18}$, whence

$$n = \frac{8.8}{8.8-6.1} = 3.25 \approx 3$$

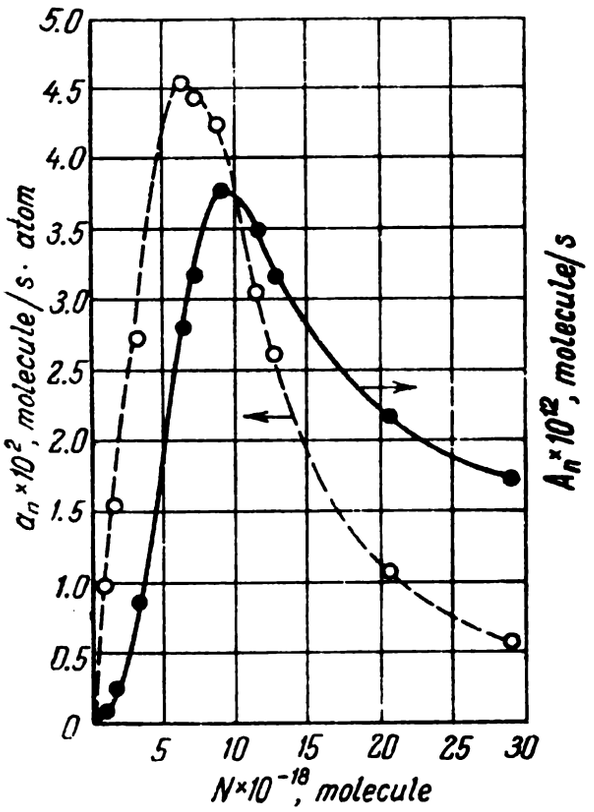



Fig. 13.10. Dependence of activity on catalyst concentration on support

Consequently, the synthesis of ammonia proceeds on triatomic ensembles of iron $[Fe]_3$.

The number of migration regions is equal to

$$Z_0 = (8.8 - 6.1) \times 10^{18} = 2.7 \times 10^{18}$$

To calculate the absolute activity $r_n$ of one $n$-atomic centre it is convenient to use the logarithmic form of Eq. (13.35):

$$\log \frac{A_n}{N^n} = \log \left( r_n Z_0^{1-n} \frac{1}{n!} \right) - \frac{N}{2.3 Z_0} \tag{13.50}$$

If the value of $n$ has been determined correctly, the experimental points in the coordinates of Eq. (13.50), i.e. $\log A_n/N^n$ versus $N$, should be plotted on a straight line, the tangent of whose angle of inclination makes it possible to define the value of $Z_0$ more precisely, and the section cut off on the axis of abscissas makes it possible to calculate $r_n$.

From the tangent of the angle of inclination of the experimental straight line we have

$$\frac{1}{2.3 Z_0} = \frac{1.96}{14 \times 10^{18}} \quad \text{or} \quad Z_0 = \frac{14 \times 10^{18}}{2.3 \times 1.96} = 3.1 \times 10^{18}$$

From the section cut off on the axis of abscissas we get

$$\log \left( r_n Z_0^{1-n} \frac{1}{n!} \right) = \overline{39}.960$$

or

$$r_n (3 \times 10^{18})^{-2} \frac{1}{1 \times 2 \times 3} = 9.12 \times 10^{-39}$$

whence

$$r_n = 9 \times 6 \times 9.12 \times 10^{36} \times 10^{-39} = 0.49 \text{ molecule/ensemble} \cdot \text{s}$$

The theory of active ensembles thus makes it possible, on the basis of an experimental relation between the activity and the concentration of the catalyst on the surface of the support, to determine the number $n$ of atoms in an active centre, the number $Z_0$ of migration regions and the absolute efficiency $r_n$ of an active centre for a given process. This method was used to study a great number of different processes proceeding on adsorption catalysts. The data for some of them are given in Table 13.1.

TABLE 13.1

**Composition of Active Centres of Selected Processes Determined according to the Theory of Active Ensembles**

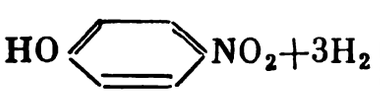
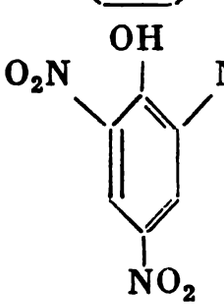
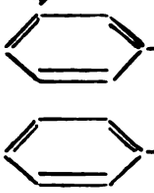
| Process | Catalyst | Support | Active centre | $r_n$, molecule/ensemble·s |
|---|---|---|---|---|
| | | *Oxidizing Processes* | | |
| $2SO_2 + O_2 \rightleftharpoons 2SO_3$ | Pt, Pd | Alumina gel<br>Silica gel | $[Pt]_1$, $[Pd]_1$ | 0.85 |
| $4NH_3 + 5O_2 \rightleftharpoons 6H_2O + 4NO$ | Pt | Alumina gel<br>Silica gel | $[Pt]_1$ | — |
| $2H_2 + O_2 \rightleftharpoons 2H_2O$ | Pt | Alumina gel<br>Carbon | $[Pt]_1$ | 0.54 |
| | | *Reduction Processes* | | |
|  $+3H_2$ | Pt | Carbon | $[Pt]_1$ and $[Pt]_5$ | — |
|  $+9H_2$ | Pt | Carbon | $[Pt]_1$ and $[Pt]_5$ | — |
| $CH_3COCH_3 + H_2$ | Ni | Magnesium oxide | $[Ni]_1$ | — |
| | | *Hydrogenation of Unsaturated Compounds* | | |
| $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ | Pt | Silica gel | $[Pt]_2$ | 5.3 (100 °C)<br>13.5 (150 °C) |
| $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ | Pt | Alumina gel | $[Pt]_2$ | 17.5 (100 °C)<br>22.2 (150 °C) |
| $C_7H_{14} + H_2 \rightleftharpoons C_7H_{16}$ | Pt | Silica gel | $[Pt]_2$<br>$[Pt]_6$ | 0.75<br>5.48 |

Table 13.1 (*concluded*)

| Process | Catalyst | Support | Active centre | $r_n$, molecule/ensemble·s |
|---|---|---|---|---|
| $+H_2$ | Pt | Silica gel | $[Pt]_2$<br>$[Pt]_6$ | 0.59<br>1.81 |
| $+2H_2$ | Pt | Silica gel | $[Pt]_2$<br>$[Pt]_6$ | 0.53<br>3.44 |
| $+3H_2$ | Pd | Silica gel | $[Pd]_2$ | — |
| $+3H_2$ | Ni | Magnesium oxide | $[Ni]_2$ | — |
|  $+H_2$ | Pt | Silica gel | $[Pt]_2$<br>$[Pt]_6$ | 1.95<br>1.18 |
| *Decomposition of* $H_2O_2$, *Synthesis of* $NH_3$ | | | | |
| $2H_2O_2 = 2H_2O + O_2$ | Pt | Silica gel | $[Pt]_1$<br>$[Pt]_3$ | 2.1<br>— |
| | | Carbon | $[Pt]_5$ | 21.5 |
| $3H_2 + N_2 = 2NH_3$ | Fe | Carbon | $[Fe]_3$ | 49.5 |
| | | Alumina gel | | 0.49 |

In addition to simple cases like the one considered above, activity curves were found that have several maxima depending on the composition. Active centres having different compositions for the same process correspond to this more complicated case. According to the law of distribution of the catalyst atoms over the surface of the support [Eq. (13.31)], the formation of the maximum number of ensembles of a certain composition corresponds to a maximum activity. Thus we can also determine the composition of the complex centres in this case by plotting the dependence of the experimentally obtained activity on the average number of catalyst atoms in a migration region $\nu = N/Z_0 = s\theta_c$. Here the number of migration regions should be found either according to data for the simplest process conducted on the same catalyst or from logarithmic equation (13.54), applying it to the separate maxima of the polyextremal curve.

Figure 13.11 shows an example of such a relation. Three processes were conducted on the same catalyst (platinum) supported on silica gel, namely: decomposition of hydrogen peroxide

$$2H_2O_2 = 2H_2O + O_2$$

hydrogenation of cyclohexane

$$C_6H_{10} + H_2 = C_6H_{12}$$

hydrogenation of benzalaniline

$$C_6H_5CH = NC_6H_5 + H_2 = C_6H_5CH_2NHC_6H_5$$

The first maximum of the total activity in the decomposition of hydrogen peroxide makes it possible to determine $Z_0$, since the curve of the specific activity in this region exponentially drops, indicating a monoatomic ensemble of platinum as the first active centre. Plotting of the relation $A_n = f(N/Z_0)$ shows

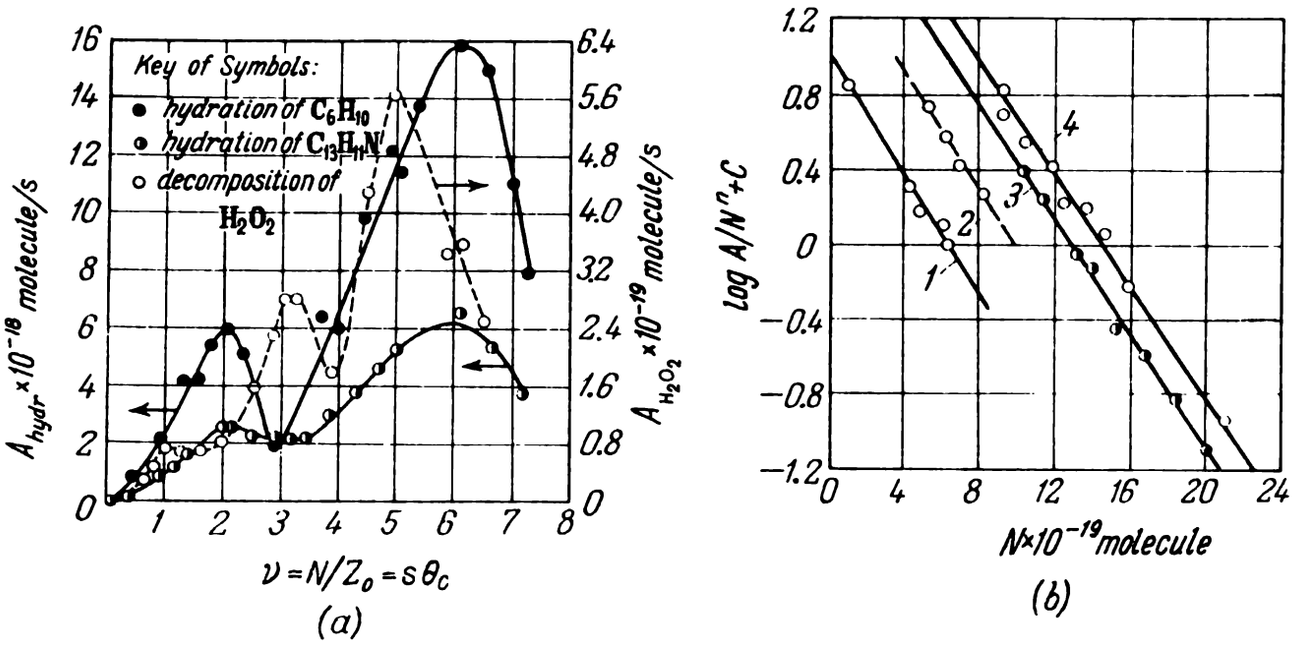



Fig. 13.11. Dependence of activity on concentration of platinum on surface of silica gel in decomposition of hydrogen peroxide and hydrogenation of C=C (cyclohexane) and C=N (benzalaniline) bonds:

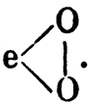
*a*—$A$ vs $\nu = N/Z_0 = s\theta_C$; *b*—log $A/N^n+C$ vs $N$; *1*—hydrogenation of $C_6H_{10}$ ($n = 2$, $C = 21$); *2*—decomposition of $H_2O_2$ ($n = 3$, $C = 40$); *3*—hydrogenation of $C_{13}H_{11}N$ ($n = 6$, $C = 102$); *4*—hydrogenation of $C_6H_{10}$ ($n = 6$, $C = 102$)

that ensembles of platinum of an odd composition $[Pt]_1$, $[Pt]_3$ and $[Pt]_5$ are active for decomposition of the peroxide, and ensembles of an even composition $[Pt]_2$ and $[Pt]_6$ are active for both cases of hydrogenation.

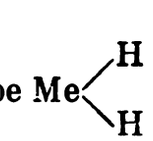
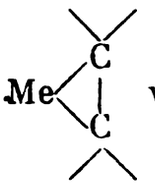
Let us check the correctness of these conclusions on a logarithmic diagram. A linear relation is obtained for a triatomic centre in the decomposition of hydrogen peroxide, for a diatomic one in hydrogenation of cyclohexane, and for a hexatomic one in hydrogenation of cyclohexane and benzalaniline. The fact that the straight lines are parallel, which gives coinciding values of $Z_0$, indicates the correctness of the calculation of this quantity from the first maximum of the activity for the decomposition of hydrogen peroxide. Other methods also exist for calculating the composition of complex active centres according to the maxima of the polyextremal activity curves.

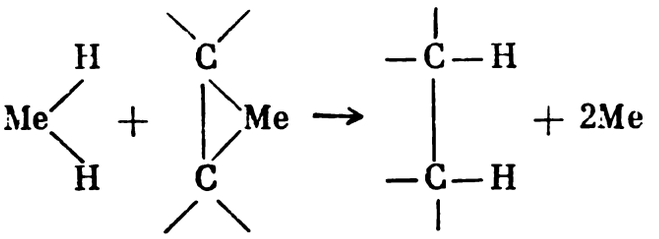
Table 13.1 gives selected data obtained in studying the composition of active centres of adsorption catalysts according to the theory of active ensembles. The catalysts used were platinum, palladium, nickel, iron, and also a number of other, for example ionic, catalysts. The catalysts were supported on silica gel, alumina gel and activated carbon. Magnesium oxide, barium oxide, cadmium oxide, metallic cadmium and nickel (on platinum) were also used. The catalytic processes studied can be divided into the following groups: oxidation, reduction

of oxygen-containing groups, hydrogenation of unsaturated bonds, decomposition of $H_2O_2$, synthesis of ammonia. In all cases the dependence of the activity on the concentration of the catalyst on the support corresponded to the theoretical one and made it possible to determine the composition of the active centre.

For oxidation processes (the oxidation of sulphur dioxide on platinum and palladium, the oxidation of ammonia, the catalysis of detonating gas) a monoatomic ensemble was found to be active in all cases. This is apparently explained as follows. The main limiting step in an oxidation process is the activation of oxygen. It can be carried out with the formation of a surface intermediate of the type  . A platinum atom can be in the valence states $5d^96s^1$, $5d^{10}6s^0$ and $5d^86s^2$. A single (on the surface) atom in the first of these states has two free valences and can form an intermediate with oxygen. The two latter states do not have free valences, but the possibility is not excluded that single atoms will become activated in the course of the process itself. If there is a non-monoatomic ensemble on the surface, then in the active state as a result of spin interaction between the *s*- and *d*-shells of adjacent atoms of the ensemble these shells mutually saturate their valences, and the formation of an intermediate will be difficult (if not excluded). For this reason a monoatomic ensemble is the active centre in the oxidation with oxygen.

In reduction processes (the reduction of the nitro group in nitrophenol and picric acid on platinum, the reduction of the carbonyl group in acetone) a monoatomic ensemble is also the main active centre. In addition, a more complicated structure—a pentatomic ensemble $[Pt]_5$—was also found to be active in platinum catalysts. The mechanism of the reaction in this case is still not quite clear and requires further studying.

For the hydrogenation of unsaturated compounds (hydrogenation of the bonds C=C and C≡C in an open and a side chain, of the bond C=C in cyclic compounds, hydrogenation of a C=N bond) the diatomic ensemble $[Me]_2$ is the active centre. A single atom of a metal in a valence-active state can easily form intermediates of the type  and  with molecules of hydrogen and unsaturated hydrocarbons. But to carry out the reaction, i.e. for the corresponding redistribution of the bonds to occur, namely,



it is necessary that both atoms be at a sufficiently close distance ensuring interaction in the intermediate complex. The metal duplet, however, is probably in the valence-saturated state. For this reason it must be activated in the course of the process, for example in the exothermic formation of an intermediate with hydrogen. As a result valences of the second atom of the duplet are freed, and it is capable of reacting with the double bond of a molecule being hydrogenated.

In odd ensembles the intermediate, firstly, does not free valences of other atoms and, secondly, screens the entire ensemble as a whole.

In addition to the metal duplet $[Me]_2$ a hexatomic ensemble is also active in processes of hydrogenation, at least on platinum. The formation of a hexatomic centre is not necessarily due to a reaction in a six-membered ring, as required by

the sextet model in the multiplet theory. Thus, the activity of the ensemble $[Pt]_6$ was discovered both in hydrogenation of cyclohexane, benzene and toluene and in hydrogenation of heptene, maleic acid, dimethylacetylenyl-carbinol (the bond C≡C) and benzalaniline (the bond C=N). Apparently, a simple geometrical correspondence between an active centre and a reacting molecule does not yet determine the composition of the centre. To determine the composition of an active centre it is also necessary to take into account the number and nature of the bonds broken and those formed as a result of the reaction. Thus, the synthesis of ammonia proceeds on a triatomic ensemble of iron $[Fe]_3$. Although the transforming molecules are simple ones, four bonds must be broken in the course of the reaction and six new ones formed. The sufficiently complicated and specific triatomic active centre corresponds to this case.

**13.7. Catalytic Properties of Transition Metals of the Periodic System.** The elements of group VIII of the periodic system have the most characteristic catalytic properties among the metals. The catalysts for a number of processes are iron (the synthesis of ammonia), cobalt, nickel, iridium, platinum, palladium (hydrogenation and for the last two—oxidation of sulphur dioxide). The metals of group VIII are also catalysts in other processes such as the decomposition of hydrogen peroxide, the preparation of detonating gas, the oxidation of ammonia, methanol, methane and carbon monoxide, and dehydrogenation of alcohols. The neighbouring elements (in the periodic system) also have catalytic activity. These include copper, silver, partly gold and possibly zinc and cadmium.

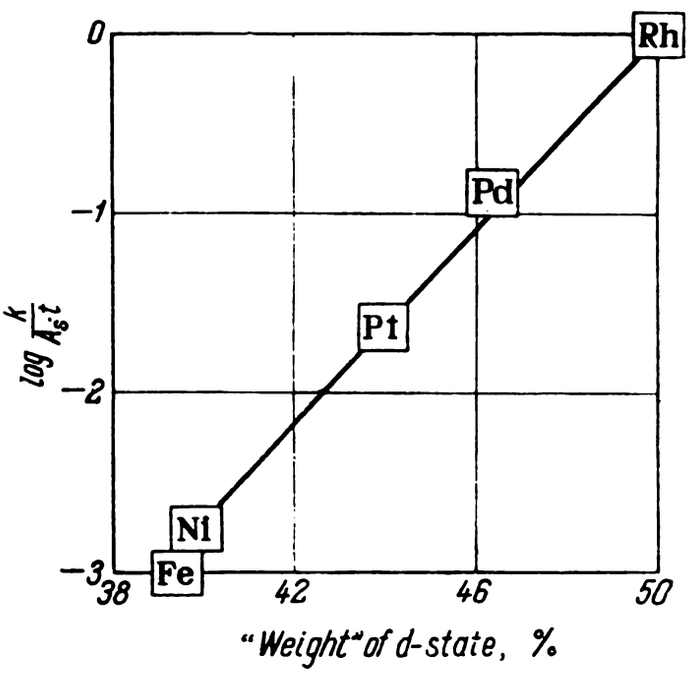



Fig. 13.12. Relation between catalytic activity and "weight" of *d*-state in hydrogenation of ethylene on transition metals

The logarithms of the specific efficiency of a catalyst—the rate constant·$cm^{-2}\cdot s^{-1}$ are laid off along the axis of ordinates

A feature of the elements listed above is the incompleteness of their electron *d*-shells, which determines the chemical and many physical properties of these elements. Characteristic of these elements is the fact that the transition of electrons from the outer *d*-shells to the outer *s*-shell (or vice versa) leads to the formation of free valences. For example, for platinum the transition from the state $5d^86s^2$, considered as the basic one, to the state $5d^96s^1$ leads to the formation of two free valences (two unpaired electrons).

A comparison of catalytic activity with electron properties shows that the activity is closely related to the presence of a free valence at the surface of the metal atoms. For crystalline catalysts the rela-

tive number of free valences (the "weights" of the *d*-states) can be approximately calculated according to L. Pauling. In Fig. 13.12 this quantity is compared with the experimentally determined catalytic activity in the hydrogenation of ethylene.

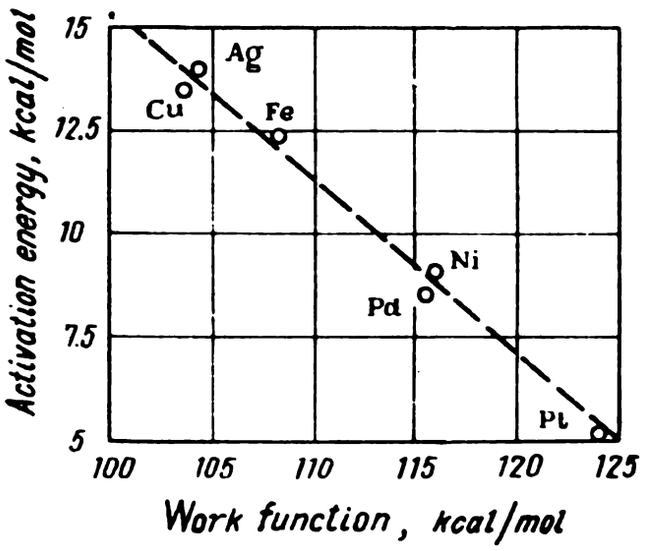



Fig. 13.13. Dependence of activation energy of deuterium exchange in ammonia on work function of an electron

It is quite possible that the determining step for some processes is either the transition of an electron from the catalyst to the reactants or, conversely, the giving of an electron of a reacting molecule to the catalyst. The mechanism of catalytic deuterium exchange in ammonia is apparently of such a nature. The determining step here consists in the reaction

$$\frac{1}{2}\,D_2 + NH_3 - e \longrightarrow NH_3D^+$$

In this case acceleration of the reaction should be expected with an increase in the affinity of the metal to an electron. The latter quantity is sufficiently accurately characterized by the work fun-

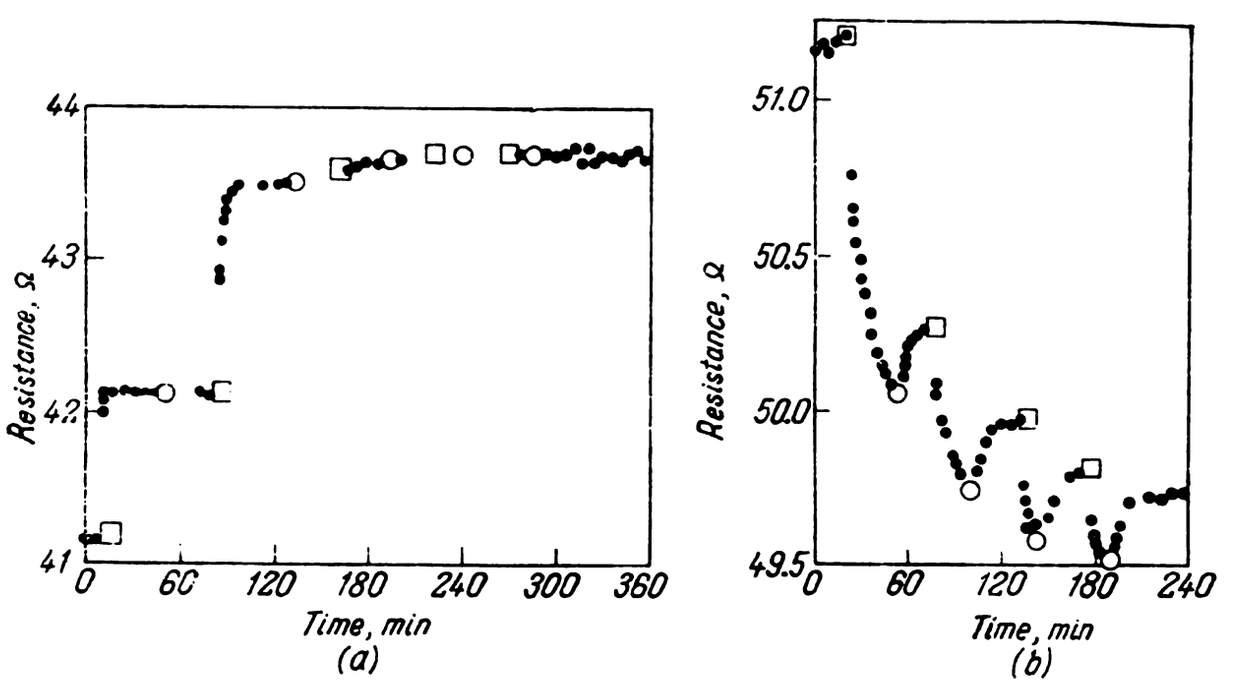



Fig. 13.14. Change in resistance of transparent nickel film ($9 \times 10^{16}$ atoms per cm$^2$): *a*—in adsorption of oxygen at 90.5 K; *b*—in adsorption of hydrogen at 294.3 K Symbols: □—inlet of gas; ○—evacuation of gas; ●—experimental points

ction of an electron in the metal lattice. The data given in Fig. 13.13 show that the theoretical assumption is quite justified.

The necessity of agreement between the electron properties of the catalyst and the reactants can be verified by direct experiments.

Figure 13.14 contains data on the change in the electrical resistance of a metal (nickel) film when oxygen (*a*) and hydrogen (*b*) are adsorbed on it. In the former case the resistance sharply grows, and in the latter it drops. In the adsorption of hydrogen, the formation of a chemisorption compound leads to the transition of an electron from the hydrogen to the conduction band of the metal. In the adsorption of oxygen, on the contrary, an oxide film is retained on the surface of the metal owing to the transition of part of the electrons from the conduction band to the valence shell of the adsorbed oxygen atoms.

Not only the mechanism of adsorption, but also that of catalysis can sometimes be observed by measuring the resistance of a metal film. Figure 13.15 shows the corresponding curves for hydrogenation of butadiene on a nickel film:

$$C_4H_6 + 2H_2 = C_4H_{10}$$

When the butadiene-hydrogen mixture (1:2) is admitted, the resistance sharply drops. Since at sufficiently high temperatures unsaturated hydrocarbons adsorbed on a metal film increase its resistance, as a rule, and hydrogen reduces its resistance, hydrogen is therefore mainly adsorbed on nickel. During the course of the reaction the resistance grows somewhat. It is the most probable that the hydrogen used in hydrogenation is partly again replenished by molecules of hydrogen adsorbed from the gaseous phase, while part of the surface is covered by molecules of butane not affecting the resistance of the film. The absence of a jump in the resistance when the butadiene-hydrogen mixture is admitted into the apparatus indicates that, apparently, the butadiene is not adsorbed in the presence of hydrogen and the reaction of catalytic hydrogenation is between the adsorbed atoms of hydrogen and the molecules of butadiene from the gaseous phase.

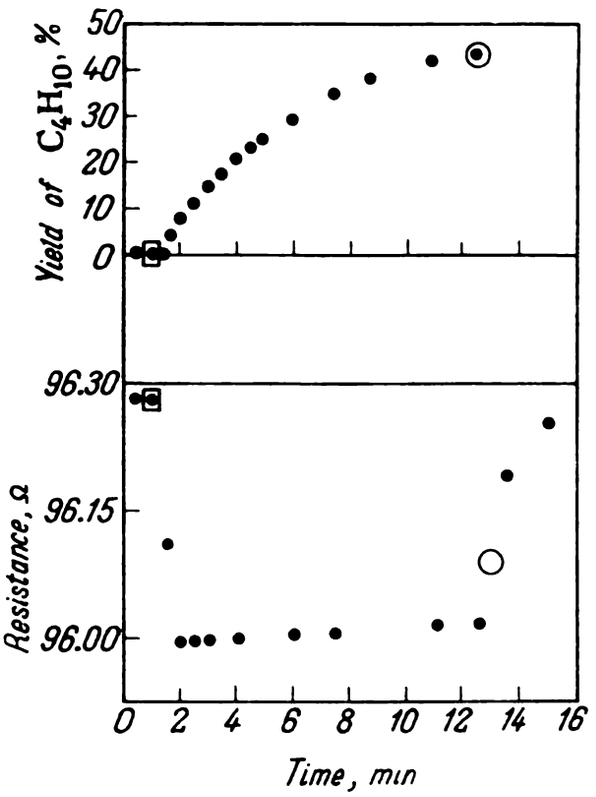



Fig. 13.15. Change in resistance of transparent nickel films in hydrogenation of butadiene at 473 K
Symbols: □—inlet of butadiene; ○—evacuation of butadiene; ●—experimental points

Lately doubts appeared as to the exclusive role played by the incompleteness of the *d*-shells of catalyst atoms. This is the result of the fact that metal catalysts were discovered whose atoms do not have incomplete *d*-shells. Such, for example, are germanium

catalysts, whose catalytic properties were proved by S. Roginsky and his collaborators.

**13.8. Catalytic Properties of Semiconductors.** Lately the theoretical explanation of the catalytic properties of semiconductors has become an important constituent part of the general theory of catalysis. In the Soviet Union the investigations of F. Wolkenstein were devoted to these problems, and we shall briefly stop to consider them.

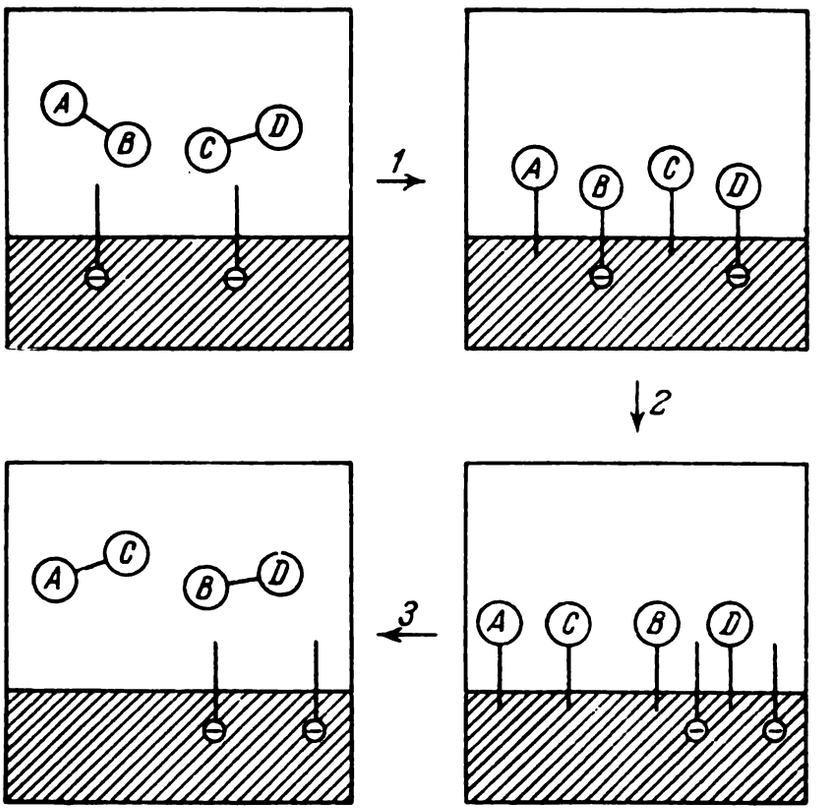



**Fig. 13.16. Diagram of heterogeneous catalytic reaction of exchange on a semiconductor:**

*1*—dissociative interaction of reacting molecules with free valences of semiconductor surface with the formation of "weakly"—A and C—and "strongly"—B and D—adsorbed radicals on the surface; *2*—transition of a strong bond into a weak one; *3*—surface reaction between radicals "weakly" bound to the surface with the formation of molecules of the products and their following desorption

The basic limiting model of the theory is an ideal crystal. At a definite temperature $T$ it has a thermodynamically equilibrium number of defects corresponding to this temperature. At any temperature differing from absolute zero, the conduction band of such a crystal contains a certain number of electrons that cause the formation of free valences on the surface of the crystal. The number of free valences grows with the temperature, the height of the activation barrier for the assumed model being determined by the width of the forbidden band for the given crystal.

The presence of a free valence on the surface of the crystal is the cause of adsorption interaction between it and molecules in the

gaseous (or liquid) phase. The nature of this bond may be as follows: (1) a *weak homopolar bond* is formed when a valence electron of an adsorbed atom is drawn into the conduction band; (2) a *strong homopolar bond* is formed when an electron passes from the conduction band to a local level formed by an adsorbed atom linked by a weak bond to the surface; (3) an *ionic bond* is formed when an electron of an adsorbed atom passes into the lattice. This scheme assumes that in the process of adsorption a molecule reacting with the surface dissociates. A strong homopolar bond and an ionic bond are states with a saturated valence, while with a weak homopolar bond the free valence remains unsaturated. Theoretically all three kinds of bond can transform into one another. From the standpoint of the surface reactions between the adsorbed particles, the weak homopolar bond will naturally be characterized by the greatest activity.

Let us consider an exchange reaction of the type

$$AB + CD \rightarrow AC + BD$$

Each of the initial molecules interacting with a free valence of the surface (Fig. 13.16) forms particles of which one is linked by a weak and the other by a strong homopolar bond to the surface. Interaction between the particles linked by a weak bond may lead to the formation of a product. Particles linked by a strong bond, as a result of preliminary transition into a state with a weak bond, are also capable of chemical interaction.

The application of electron notions to heterogeneous catalysis leads to interesting, though meanwhile only qualitative results. The latter show that catalytic activity is related to the electron state of the catalyzing surface. It should be remembered, however, that all the assumptions are based on ideal crystals. For this reason the conclusions of the electron theory are applicable only in the limit case and meanwhile cannot be compared quantitatively with experimental data. The rapid development in recent years of this branch of the theory of catalysis gives rise to hope that the near future will see the appearance of variants of the electron theory of catalysis which are comparable with experimental results.

CHAPTER 14

# INVESTIGATING THE MECHANISM AND KINETICS OF CHEMICAL REACTIONS BY THE METHOD OF TRACER ATOMS

**14.1. General.** Tracer atoms (tracers) open broad possibilities for the direct investigation of the mechanism of a chemical reaction. Both stable and radioactive isotopes may be used for this purpose. Usually a definite atom in a molecule being investigated is replaced by a tracer (an atom of a stable or radioactive isotope), namely, the atom that changes its position, and its transformations as a result of the reaction are investigated.

The possibility of using radioactive atoms as indicators is determined by two features of these atoms. Up to their disintegration radioactive atoms in a chemical respect do not practically differ in any way from the basic non-radioactive ones. After disintegration the properties of the atoms change, but the radiation emitted makes it possible to detect the disintegrating atoms. Methods of detecting radioactive atoms have reached a high degree of perfection at present, and the sensitivity of the corresponding instruments is very high. It is quite a simple matter to detect $10^{-16}$ gramme of radioactive iodine ($^{131}I$) with a half-life of 8.0 days using a Geiger counter.

This method has its limitations, however, if the radiation of the radioactive isotope affects the proceeding processes or if the quantitative differences in the proceeding of processes with and without the participation of isotope molecules are sufficiently great. True, no account may be taken of these limitations in investigating the majority of chemical processes.

Besides, a convenient radioactive atom of a given element having a sufficiently great half-life is not always available. In such cases it is more convenient to use stable isotopes. It is also convenient to use them when it is necessary to completely exclude the influence of radiation on a process.

**14.2. Use of Tracers to Establish Place of Bond Breaking in a Molecule.** Tracer atoms can be used with great success to establish what bonds break as a result of a chemical process. Back in 1934 M. Polanyi and Z. Szabo first used heavy oxygen $^{18}O$ to find the place of breaking of the bonds in the reaction of hvdrolysis of esters. Two kinds

of reactions can be written for this process:

$$RCOO\boxed{R' + H\overset{\star}{O}}H \rightleftharpoons RCOOH + H\overset{\star}{O}R'$$

$$RCO\boxed{OR' + H\overset{\star}{O}}H \rightleftharpoons R\overset{\star}{C}OOH + HOR'$$

The hydrolysis of amyl acetic ester was conducted with water containing heavy oxygen $^{18}O$, which is marked with a star in the reaction equations, in an alkali medium. If a reaction follows the first equation, the result should be an alcohol containing heavy oxygen. If it follows the second equation, the alcohol formed will contain no heavy oxygen. The alcohol separated from the products and subjected to hydration produced water having a normal density. Thus the experiment showed that the reaction followed the second equation. Similar results were obtained in the hydrolysis of monomethyl ester of amber acid.

Studying of the esterification of benzoic acid with methyl alcohol containing heavy oxygen in an acid medium showed that the water formed does not contain the oxygen isotope $^{18}O$. Since it was established by separate experiments that the oxygen of the benzoic acid is exchanged slowly, the following equation of the reaction of esterification may be assumed:

$$C_6H_5CO\boxed{OH + H}{}^{18}OCH_3 \rightleftarrows C_6H_5CO^{18}OCH_3 + H_2O$$

It was found that this is a first-order reaction (the same as a reaction of isotope exchange) relative to the difference in concentrations of $^{18}O$ in the reagents, and that its rate is directly proportional to the hydrogen ion concentration.

Different isotopes can be used, depending on the type of reaction being studied, to establish the places of bond breaking and the nature of movement of the atoms, as already indicated at the beginning of the present chapter. For example, the radioactive carbon isotope $^{11}C$ was used to determine the carbon atoms of propionic acid which carbon dioxide is formed from in the oxidation of the acid with a permanganate in an alkaline medium. As a result of oxidation, carbon dioxide and oxalic acid are formed. The reaction can proceed in two ways, namely

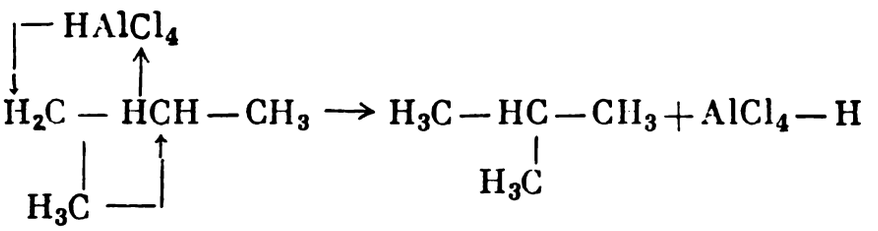
$$\overset{\beta}{C}H_3\overset{\alpha}{C}H_2\overset{\star}{C}OOH \longrightarrow \overset{\beta}{C}O_2 + HOO\overset{\alpha\star}{C}COOH$$

$$\overset{\beta}{C}H_3\overset{\alpha}{C}H_2\overset{\star}{C}OOH \longrightarrow HOO\overset{\beta\alpha}{C}COOH + \overset{\star}{C}O_2$$

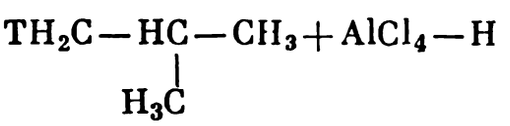
According to the first way the $CO_2$ is formed from the beta-carbon of the ethyl group, according to the second one—from the carboxyl

carbon. It was found that the oxidation simultaneously proceeds in both ways, but at a different rate: 75% of the carbon dioxide is formed in the first way, and 25% in the second one. Depending on the pH of the solution, the part played by each of the ways in the formation of the $CO_2$ changes. Oxidation with a chromium mixture leads to the formation of all the $CO_2$ in the second way.

The use of radioactive tritium made it possible to gain an understanding of the reaction of isomerization of butane into isobutane in the presence of a complex of an aluminium trichloride and hydrogen chloride catalyst. It was assumed that the process proceeds as follows




This mechanism was confirmed by using a catalyst in which an atom of hydrogen was replaced by one of tritium, since under the action of such a catalyst the products obtained were




The use of the carbon isotope $^{13}C$ made it possible to trace the migration of atoms into a molecule in the presence of certain catalysts. For example, the migration of carbon into propane in the presence of $AlBr_3$ was shown:

$$^{13}CH_3 - CH_2 - CH_3 \longrightarrow CH_3 - {}^{13}CH_2 - CH_3$$

Radioactive carbon was used to verify the assumption that in the synthesis of high-molecular hydrocarbons from CO and $H_2$, methane (present in the gas mixture) in the presence of a catalyst may enter into the composition of more complicated hydrocarbons. After several hours of circulation of a mixture of 50% of methane with $^{14}C$ tracers and 50% of CO + $H_2$ over an iron catalyst, the radioactivity of the methane did not practically change, and that of the carbon monoxide obtained by combustion of the synthesis products was insignificant. This indicates that the methane does not practically participate in the reaction.

To verify the assumptions that the synthesis of hydrocarbons from CO and $H_2$ proceeds through the alternating formation and reduction of a metal carbide, a considerable amount of radioactive iron carbide was introduced into the iron catalyst. Experiments showed that not over 10% of the entire product is formed through the carbide (P. Emmett).

An ion-exchange reaction, as shown by F. Long, can be used to study the structure of complex compounds. The ion exchange can indicate the nature of the bond in the complex compounds. Thus, if we investigate the exchange of trivalent metals with complex compounds of oxalic acid having the general structure $A_3M(C_2O_4)_3$, where A is an alkali metal and M a trivalent one, we can establish the nature of the bond of the trivalent metal with an ion of oxalic acid. This bond may be either covalent or ionic. In the latter case the tracer ions of the oxalic acid in the solution should exchange places with the oxalic acid ions in the

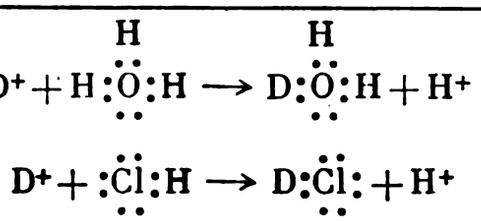
complex salt. If the bond is a covalent one, such an exchange should not be observed. A tracer oxalate ion usually contains radioactive carbon $^{14}C$. If, for example, we take potassium chromioxalate $K_3[Cr(C_2O_4)_3]$ and potassium ferric oxalate $K_3[Fe(C_2O_4)_3]$ as the complex compounds and investigate the ability of such compounds to exchange their oxalate ions with potassium oxalate $K_2\overset{*}{C}_2O_4$ having tracer carbon atoms, it is found that the oxalate ions in the complex compound containing iron are easily exchanged, while in the complex compound containing chromium the exchange proceeds very slowly at room temperature. In this way the ionic nature of the bond in the first case and the covalent nature in the second one were proved. Similar investigations of oxalate ion exchange between oxalic acid and trioxalate complexes of cobalt and aluminium showed that the bonds in the cobalt complexes are covalent and in the aluminium complexes ionic.

**14.3. Isotope Exchange Reactions.** Before using tracer atoms to study separate reactions, it is necessary to determine whether simple exchange reactions take place with the participation of these atoms, i.e. such reactions when the tracer atom of a given compound changes places with a non-radioactive istotope atom of the same or a different compound, since this may distort the final results. In this connection a great number of exchange reactions were studied with inorganic and organic substances. Enormous experimental data have been accumulated in this field to date. We shall briefly consider only exchange reactions of hydrogen and oxygen and the general equation of the kinetics of isotope exchange reactions.

Hydrogen atoms of various compounds easily change places with deuterium atoms of heavy water. The hydrogen atoms occupying different positions in a molecule of the compound are replaced by deuterium at a different rate. For example, it was established that this exchange proceeds rapidly in compounds where the hydrogen atoms are combined with a halogen, sulphur, oxygen, selenium, tellurium, phosphorus or nitrogen. Hydrogen combined with carbon either does not change places with deuterium at all or does this very slowly. For example, in formic acid the hydrogen atoms of carboxyl groups change places at a very high rate, while the hydrogen atoms bound to carbon atoms do this at an exceedingly low rate. If the hydrogen of the carboxyl group is replaced by a metal, the exchange of the hydrogen bound to the carbon also proceeds at a very low rate.

Experiments have shown that a rapid exchange of the hydrogen atoms is observed only in compounds having free electron pairs. Isotope exchange in ammonia, water and hydrogen chloride can be depicted as follows:

$$D^+ + \begin{array}{c} H \\ \cdot\cdot \\ :N: \\ \cdot\cdot \\ H \end{array} H \longrightarrow D:\begin{array}{c} H \\ \cdot\cdot \\ N: \\ \cdot\cdot \\ H \end{array} + H^+$$



i.e. a deuterium ion joins a free electron pair and simultaneously or immediately after this a hydrogen atom breaks away from another electron pair. This process is not associated with the surmounting of a considerable potential barrier, and for this reason it can proceed quite rapidly at moderate temperatures. When the exchange of the hydrogen atoms involves breaking of existing bonds, as, for example, the exchange of hydrogen atoms bound to a carbon atom, the process is characterized by a considerable activation energy. This is why it proceeds at a sufficiently high rate only at elevated temperatures or, if the temperature is moderate, in the presence of catalysts.

The investigation of oxygen exchange reactions in inorganic salts gives valuable information on the relative strength of the bond of the oxygen atoms with the non-metallic anion atoms. Usually the exchange of oxygen atoms between an anion and water containing $^{18}O$ is studied. Experiments show that the rate of exchange in carbonic, boric and sulphuric acids, in neutral solutions of molybdates ($MoO_4^{2-}$), tungstates ($WO_4^{2-}$), arsenites ($AsO_2^-$), arsenates ($HAsO_4^{2-}$), chromates ($CrO_4^{2-}$), bichromates ($Cr_2O_7^{2-}$), metaborates ($BO_2^-$), pyroborates ($B_4O_7^{2-}$), thiosulphates ($S_2O_3^{2-}$), metabisulphates ($S_2O_5^{2-}$), and selenites ($SeO_3^{2-}$) is high. It is lower in carbonates ($CO_3^{2-}$), bicarbonates ($HCO_3^-$), bromates ($BrO_3^-$), iodates ($IO_3^-$), silicates ($SiO_3^{2-}$). No exchange reactions practically occur in nitrates ($NO_3^-$), nitrites ($NO_2^-$), chlorates ($ClO_3^-$), perchlorates ($ClO_4^-$), sulphates ($SO_4^{2-}$), selenates ($SeO_4^{2-}$) and phosphates ($PO_4^{3-}$, $HPO_4^{2-}$ and $H_2PO_4^-$). The rate of an exchange reaction frequently depends to a considerable degree on the pH of the medium. Alkalies accelerate exchange in bichromates, chlorates and iodates, but appreciably inhibit exchange in chromates, nitrates, sulphates and thiosulphates. Acids accelerate exchange in chromates, chlorates and nitrates. It has been established for organic oxygen compounds that the rate of exchange of the oxygen of the carbonyl and carboxyl groups depends on the acidity of the medium. It is interesting to note that an increase in the strength of the acid facilitates exchange. This can be seen on the example of acetic, monochloroacetic and trichloroacetic acids. The rate of exchange grows from the acetic through the monochloroacetic to the trichloroacetic acid. The oxygen of alcohol and phenyl hydroxyl groups does not ordinarily change places. In the tertiary alcohol trianisole carbinol, exchange catalyzed by acids may be observed, however. Only one oxygen atom in sugars can be exchanged.

When exchange proceeds easily at low temperatures, i.e. does not require energy for breaking strong bonds, it involves intermediates that readily react with water. For example, the fact that exchange does not proceed in solutions of salts of strong acids and comparatively easily proceeds in solutions of salts of weak acids which form reversible oxidation-reduction systems justifies the assumption that the exchange is due to hydrolytic equilibria. For example, exchange in bichromates and pyroborates can be explained by the

possibility of the following reactions:

$$Cr_2O_7^{2-} + H_2O \rightleftarrows 2CrO_4^{2-} + 2H^+$$

$$B_4O_7^{2-} + 5H_2O \rightleftarrows 4BO_3^{3-} + 10H^+$$

In organic acids the exchange apparently proceeds according to the mechanism of a reaction of esterification, i.e.

$$R_1COOH + H^{18}OH \rightleftarrows R_1CO^{18}OH + HOH$$

The exchange of isotope atoms has also been studied on a great number of examples of isotope atoms of carbon, nitrogen, sulphur, the halogens, phosphorus, arsenic, antimony, manganese, etc. Readers can acquaint themselves with these reactions in the relevant publications.

The rate of an isotope exchange reaction

$$AX + BX^* \rightleftarrows AX^* + BX$$

obeys the equation of a bimolecular chemical reaction

$$\frac{dx}{dt} = k'(a-x)y - k''(b-y)x \tag{14.1}$$

where $a$ and $b$ = numbers of moles of substances AX and BX, respectively
$x$ and $y$ = numbers of moles of the isotope varieties $AX^*$ and $BX^*$.
The ratio

$$k'/k'' = \alpha \tag{14.2}$$

where $\alpha$ is the single separation coefficient for this reaction, equal to the equilibrium constant. The total content $r$ of isotope molecules in a given system is a constant quantity,

$$x + y = r \tag{14.3}$$

If we consider that in the majority of cases $\alpha = 1$, i.e. $k' = k''$, then by opening parentheses in Eq. (14.1) it can be transformed into the equation

$$\frac{dx}{dt} = k'[ar - (a+b)x] \tag{14.4}$$

Integration yields

$$-\ln[ar - x(a+b)] = k'(a+b)t + \text{const} \tag{14.5}$$

We find the value of the integration constant from the initial conditions, namely, $x = 0$ at $t = 0$. Inserting these values of the variables into Eq. (14.5), we get

$$\text{const} = -\ln ar \tag{14.6}$$

Introducing Eq. (14.6) into Eq. (14.5), we obtain

$$\ln\frac{ar}{ar + (a+b)x} = k'(a+b)t \tag{14.7}$$

or

$$-\ln\left[1 - \frac{(a+b)x}{ar}\right] = k'(a+b)t \tag{14.8}$$

The value of the product $ar$ can be expressed through the number of gramme-molecules of the substances AX and BX and the limiting content $x_\infty$ of molecu-

les of $AX^*$ in the mixture after it reaches an equilibrium state. When equilibrium is reached, the derivative $dx/dt$ becomes equal to zero, i.e.

$$\frac{dx}{dt}=0 \tag{14.9}$$

and accordingly the right-hand part of Eq. (14.4) becomes equal to zero, i.e.

$$ar-(a+b)\,x_\infty=0 \tag{14.10}$$

whence

$$ar=(a+b)\,x_\infty \tag{14.11}$$

The insertion of Eq. (14.11) into Eq. (14.8) yields the final equation

$$-\ln\left(1-\frac{x}{x_\infty}\right)=k'(a+b)\,t \tag{14.12}$$

or designating

$$k'(a+b)=k \tag{14.13}$$

we get

$$-\ln\left(1-\frac{x}{x_\infty}\right)=kt \tag{14.14}$$

The appearance of this equation is similar to that of a reversible first-order reaction, notwithstanding the fact that the reaction actually proceeds like a bimolecular one. Thus, in considering the dependence of the quantity $x$ on $t$, we cannot reach a conclusion on the order of a reaction for isotope exchange reactions. To determine the order of such reactions, it is necessary to find the dependence of the constant $k$ on the concentration of the molecules changing places.

**14.4. Use of Tracers to Investigate the Kinetics of Chemical Processes.** The use of isotopes in investigating the mechanism of chemical reactions makes it possible to determine the rate of formation and consumption of the intermediates, determine the sequence of formation of the intermediates, find the substances that are formed simultaneously from the same antecedent, and also to establish what bonds are broken in the course of a reaction. To properly solve the problem of the kinetics, information on the exchange reactions proceeding in the system must be available.

Tracers can be used to determine the rate constants of reactions in equilibrium. These constants are usually determined in conditions far from equilibrium. No data have been obtained to date indicating that the kinetics of a reaction will not change when approaching equilibrium. And only at present does the method of tracers open broad possibilities for determining the kinetics of the forward and reverse reactions in conditions of equilibrium. True, very little has meanwhile been done in this field. J. Wilson and R. Dickinson determined the rate of the forward and reverse reactions in equilibrium in the system

$$H_3\overset{*}{A}sO_3+I_3^-+H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_3\overset{*}{A}sO_4+3I^-+2H^+$$

The tracer atom used was $^{76}As$ with a half-life of 26.8 hours. A solution of arsenite was prepared by dissolving radioactive arsenic trio-

xide in an alkali. The solutions to be studied were mixtures of radioactive arsenite, non-radioactive arsenic acid, hydrochloric acid and potassium iodide. The degree of exchange during a given time interval was determined after maintaining equilibrium by adding water and an excess of ammonia to a sample taken from the system. The arsenate ion was precipitated in the form of magnesium-ammonium arsenate, which was then calcinated. The radioactivity of the powder produced was determined by means of an electroscope. It was shown by special experiments that no direct exchange occurs in the conditions of the reaction between $As^{III}$ and $As^{V}$. The value of the rate constant $k_2$ of the reverse reaction was computed from the rates of exchange determined at different concentrations of the reactants in the conditions of equilibrium. Here use was made of the dependence of the rate on the concentration found for the reaction of reduction of arsenic acid in conditions far from equilibrium. These values were calculated by the equation

$$J_2 = k_2\,[H_3AsO_4]\,[H^+]\,[I^-] \tag{14.15}$$

where $J_2$ is the rate of the reverse process.

The values of $k_2$ obtained in this way were found to be sufficiently stable (they ranged from 0.06 to 0.082). The mean value of $k_2$ equal to 0.071 $dm^6/mol^2 \cdot min$ at 25 °C was close to the value of $k_2$ (0.057 $dm^6/mol^2 \cdot min$) obtained in conditions far from equilibrium. The activation energy determined in equilibrium and equal to 14.1 kcal/mol was close to the value (14.5 kcal/mol) obtained in conditions far from equilibrium.

The investigation of the kinetics of a chemical reaction with the use of tracers often makes it possible to directly determine the rate of formation and consumption of any intermediate of a complicated chemical reaction and thus form an opinion on the mechanism of this reaction. The method of solving this problem considered below was proposed by M. Neiman. If in the course of a complicated chemical reaction an intermediate X is formed as shown below:

$$\begin{array}{ccccccc} \ldots \longrightarrow & A_1 & & B_1 & \longrightarrow \ldots \\ & & \searrow & \nearrow & \\ & & X & & \\ & & \nearrow & \searrow & \\ \ldots \longrightarrow & A_2 & & B_2 & \longrightarrow \ldots \end{array}$$

then the differential equation characterizing the formation of this intermediate can be written as follows:

$$\frac{d\,[X]}{dt} = \sum k_i\,[A_i] - \sum k_i'\,[X] \tag{14.16}$$

Introducing the notation

$$\sum k_i\,[A_i] = J \tag{14.17}$$

$$\sum k_i' = k \tag{14.18}$$

Eq. (14.16) can be written in the form

$$\frac{d[X]}{dt} = J - k[X] \tag{14.19}$$

If we introduce a substance $X^*$ with radioactive or stable isotopes into a reaction system at a certain moment of time, the concentration of the tracer substance $X^*$ will change with time owing to the formation from the reactants $A_i$ of new amounts of the substance $X^*$ with a different content of the tracer atoms. Let us denote the specific activity of substance $A_i$ by $a_A$. Since the isotope effects are usually not great, it can be considered that the change in the concentration of substance $X^*$ with time will obey an equation similar to Eq. (14.19) with the same value of the constant $k_i$. Hence

$$\frac{d[X^*]}{dt} = J^* - k[X^*] \tag{14.20}$$

But the relative content of the radioactive isotope is characterized by the specific activity $a_X$. Therefore

$$a_X = \frac{[X^*]}{[X]} \tag{14.21}$$

Similarly we can write that

$$a_A = \frac{J^*}{J} \tag{14.22}$$

Using Eqs. (14.21) and (14.22), Eq. (14.20) can be written as

$$\frac{d[X^*]}{dt} = a_A J - k a_X [X] \tag{14.23}$$

Differentiation of Eq. (14.21) with respect to time yields

$$\frac{da_X}{dt} = \frac{\frac{d[X^*]}{dt} - a_X \frac{d[X]}{dt}}{[X]} \tag{14.24}$$

Inserting Eqs. (14.19) and (14.23) into Eq. (14.24), we get

$$\frac{da_X}{dt} = \frac{J(a_A - a_X)}{[X]} \tag{14.25}$$

In the particular case when the tracer substance $X^*$ is added to a system of inactive reactants, i.e. when $a_A = 0$, the latter equation becomes simpler, i.e.

$$\frac{da_X}{dt} = -\frac{a_X J}{[X]} \tag{14.26}$$

or

$$\frac{d \ln a_X}{dt} = -\frac{J}{[X]} \tag{14.27}$$

Separating the substance X at different moments after the addition of $X^*$ and determining its content and specific activity, we can find an empirical relation between the amount of this substance and the magnitude of its specific activity and the time, i.e.

$$[X] = f(t) \tag{14.28}$$

$$a_X = \varphi(t) \tag{14.29}$$

We can use the found relations to determine the derivatives

$$\frac{d[X]}{dt}=f'(t) \tag{14.30}$$

$$\frac{da_X}{dt}=\varphi'(t) \tag{14.31}$$

It follows from Eq. (14.26) that

$$J=F(t)=-\frac{[X]\frac{da_X}{dt}}{a_X} \tag{14.32}$$

Substitution for the quantities in this equation of their values from Eqs. (14.28), (14.31) and (14.29) gives the expression

$$J=F(t)=-\frac{f(t)\,\varphi'(t)}{\varphi(t)} \tag{14.33}$$

that can be used to compute the value of $J$, i.e. the rate of formation of the intermediate X. Knowing this quantity, we can easily find the rate of consumption of the substance X, which is determined by the quantity $k[X]$. Inserting Eqs. (14.33) and (14.30) into Eq. (14.19), we get

$$k[X]=-\frac{f(t)\,\varphi'(t)}{\varphi(t)}-f'(t) \tag{14.34}$$

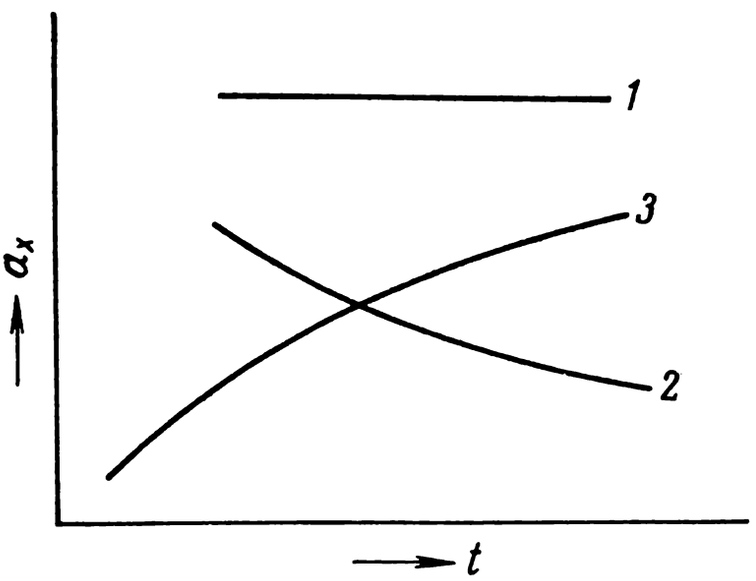



Fig. 14.1. Change in specific activity of the substance X* with time:
1—$da_X/dt = 0$; 2—$da_X/dt < 0$; 3—$da_X/dt > 0$

Figure 14.1 shows different curves of the change in the specific activity of the substance X* with time plotted according to experimental data. For curve *1* we have $da_X/dt = 0$, consequently $a_X$ = const and from Eq. (14.26) it follows that in this case $J = 0$, i.e. the intermediate is not formed, but only consumed. In a more general case the quantity $a_X$ decreases with time (curve *2*). In this case the rate of formation of the intermediate X and its consumption are calculated by Eqs. (14.33) and (14.34). If the tracer atoms are initially contained only in the substance $A_i$, then the value of $a_X$ grows with time (curve *3*).

If the concentration of the intermediate X becomes stationary, we have

$$\frac{d[X]}{dt}=0 \tag{14.35}$$

and Eq. (14.19) becomes

$$J = k[X] \tag{14.36}$$

Inserting Eq. (14.36) into Eq. (14.25), we obtain

$$\frac{da_X}{dt}=k(a_A-a_X) \tag{14.37}$$

In this case an analysis of the experimentally obtained curves showing how the specific activities $a_A$ and $a_X$ depend on the time allows us to determine the substance that is the predecessor of the intermediate X. If we add to the reaction

system the initial substance X and a tracer product A which is assumed to be the predecessor of X, we can check the correctness of this assumption according to the curves showing the time dependence of the quantities $a_A$ and $a_X$. If the predecessor of X is A, then the specific activity of A and X should change as shown in Fig. 14.2. The specific activity $a_A$ of substance A, owing to its dilution by inactive substances formed from the reactants, will decrease along curve *1* whose equation is easy to find by the procedure considered above. This equation has the form

$$\frac{da_A}{dt} = \frac{a_A J_A}{[A]} \qquad (14.38)$$

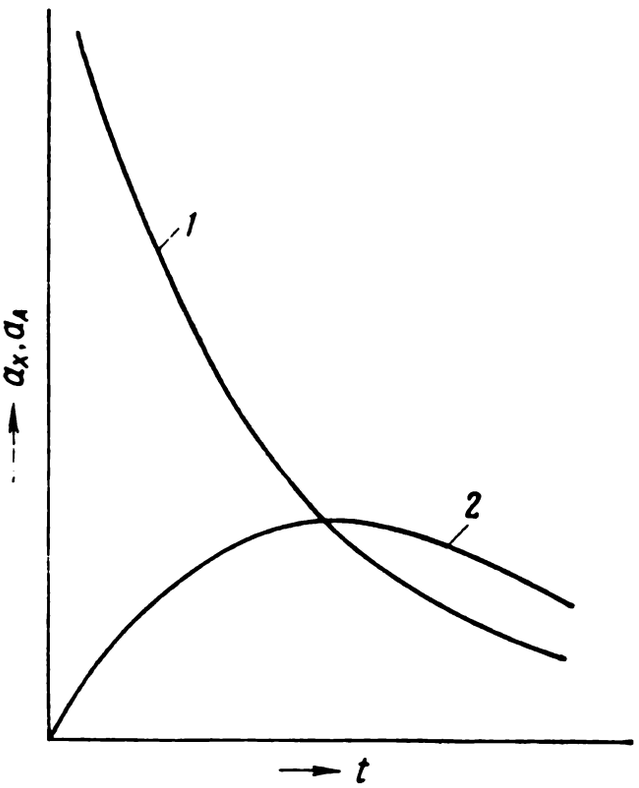



Fig. 14.2. Change in specific activities $a_X$ and $a_A$ with time:
*1*—$a_A = f(t)$; *2*—$a_X = f_1(t)$

The specific activity of substance X at the moment when the radioactive substance A is added to it is obviously equal to zero ($a_X = 0$). At all other moments the change in $a_X$ with time obeys Eq. (14.37). As long as $a_A < a_X$, the value of $da_X/dt > 0$, i.e. $a_X$ grows with time. When $a_A$ becomes equal to $a_X$, we have $da_X/dt = 0$, i.e. curve *2* passes through a maximum. During the further course of the process $a_A > a_X$, $da_X/dt < 0$ and curve *2* begins to drop. If the experimental curves showing the dependence of $a_A$ and $a_X$ on time correspond to the theoretical ones, this confirms the assumption that substance A is the initial one for the substance X.

If a stationary state is observed for a given reaction, the curves considered above can be used to find the value of $k$ and its reciprocal $\tau$—the mean lifetime of molecules of X. These quantities can be calculated in several ways. One of the simplest ones consists in the following. The difference $a_A - a_X$ is calculated for the given moment of time, and the derivative $da_X/dt$ according to the angle of inclination of the tangent. Inserting the values obtained into Eq. (14.37), we find $k$ or $\tau = 1/k$. These calculations are performed for several points, and then the mean value of $k$ or $\tau$ is determined.

The same problem can be solved by graphical integration of Eq. (14.37) or by integration of Eq. (14.38) if we can find the law of the change in $a_A$ with time from the results of experiments. Very often the following function is a quite suitable one that sufficiently well agrees with experimental data:

$$a_A = Ae^{-k_1 t} \qquad (14.39)$$

It is obvious that in principle the same method can be used to solve similar problems for more complicated reactions. For a proper solution of the problems related to the mechanism of a reaction, however, one must always be sure that no exchange reactions proceed. Such reactions may introduce considerable complications into the interpretation of the results obtained, or even make it impossible. The method discussed above was used by M. Neiman and A. Lukovnikov for establishing the possibility of the formation of carbon dioxide from carbon monoxide in the cold-flame oxidation of butane. It was shown that in this reaction insignificant amounts of $CO_2$ are formed by the oxidation of CO.

**14.5. Use of Tracers to Investigate the Surface of Solids and Heterogeneous Reactions.** Radioactive tracers can be successfully used for studying the kinetics of exchange reactions in heterogeneous systems. Among interesting reactions that could not be studied without the use of tracer atoms are the reactions of precipitates with ions in a solution, or reactions between solids (for example, metals) and ions. Isotopes can often be used with great success for investigating the properties and surface areas of finely crystalline or porous bodies.

F. Paneth back in 1922 proposed a method for determining the surface area of crystalline powders with the aid of radioactive atoms. By exchanging tracer ions of lead with the surface of a crystalline precipitate of lead sulphate, it is simple to determine the number of lead ions on the surface of the crystals, and knowing the area occupied by one lead ion, it is easy to find the total area of the powder. The area occupied by one ion of a substance on a surface can be easily computed from the distances between ions in a crystal lattice of a solid. This quantity ($l^2$) is obtained from the obvious equation

$$l^2 = \left(\frac{M}{aN_A\rho}\right)^{2/3} \tag{14.40}$$

where $M$ = mass of one mole
$a$ = number of gramme-atoms per mole of solid
$N_A$ = Avogadro constant
$\rho$ = density of substance.

The principle underlying the method of determining the surface area of a crystalline powder consists in the following. A powder of lead sulphate is agitated with a solution containing radioactive lead. As a result of the exchange of ions, exchange equilibrium sets in; the separation coefficient can be taken equal to unity with a sufficient degree of accuracy. Following the change in the activity of the solution with time and gradually stirring the mixture, we can establish the kinetics of the exchange reaction. Usually isotope exchange reactions obey a first-order equation. The degree of exchange $x$ in the time $t$ after the beginning of the exchange reaction can be found quite easily from the obvious relation

$$x = \frac{a_0 - a_t}{a_0 - a_\infty} \tag{14.41}$$

where $a_0$ = initial activity of the radioactive substance
$a_\infty$ = activity of this substance after equilibrium sets in
$a_t$ = the same in the time $t$ after the beginning of the exchange reaction.

If in a precipitate-ion or solid-ion exchange reaction only the atoms of the precipitate or the solid that are on the surface take part, and if the separation coefficient is equal to unity, we can find the mass of the substance capable of participating in the exchange reaction with the aid of the following proportion:

$$\frac{m_{\text{surface}}}{m_{\text{solution}}} = \frac{a_0 - a_\infty}{a_\infty} \tag{14.42}$$

where $m_{\text{surface}}$ = mass of the substance on the surface of the solid capable of taking part in the exchange reaction
$m_{\text{solution}}$ = mass of this substance in the solution.

The mass of the substance in the solution can be found by ordinary chemical analysis. For this reason it is easy to find from Eq. (14.42) the number of ions on the surface (the quantity $m_{\text{surface}} \cdot \frac{N_A}{A}$, where $A$ is the mass of one gramme-

ion), and knowing the dimensions of ions, it is simple to find, as already noted above, the total surface area of the crystals.

Another example of an exchange reaction between a precipitate and an ion in a solution is the reaction between the precipitate of silver chloride and silver ions, the latter being mixed with the radioactive isotope of silver $^{111}Ag$, designated $\overset{\star}{Ag}$:

$$AgCl + \overset{\star}{Ag}^{+} \rightleftarrows \overset{\star}{Ag}Cl + Ag^{+}$$

Exchange is sometimes possible not only on the surface of a solid, but also in its bulk owing to diffusion of the ions from the solution. Such a process of self-diffusion may result in uniform distribution of the radioactive substance throughout the entire system solid-liquid, and for this reason the calculations considered above will no longer be applicable.

# ELECTROCHEMISTRY

## CHAPTER 15

## FUNDAMENTALS

**15.1. Subject of Electrochemistry.** Electrochemistry is a branch of physical chemistry that studies the relation between chemical and electrical phenomena and the laws of their interaction. The main subject of electrochemistry are the processes that proceed on electrodes when a current passes through solutions (the so-called *electrode processes*). Two main branches of electrochemistry can be distinguished, namely, the *thermodynamics of electrode processes* dealing with equilibrium states of electrode-solution systems, and the *kinetics of electrode processes*, studying the laws of the proceeding of these processes with time. Electrochemistry studies not only electrode processes, however. The theory of electrolytes is also quite frequently included in this branch of physical chemistry. Not only the properties of electrolytes related to the passage of a current are studied (electrical conductance, etc.), but also other properties of electrolytes (viscosity, solvation, chemical equilibria, etc.). The theory of electrolytes can also be considered as part of the general theory of solutions, but in the present course it has been included in the part on electrochemistry.

Electrochemistry is of a very great significance, since the laws of electrochemistry are the theoretical basis for the development of important technical processes—*electrolysis* and *electrosynthesis*, i.e. the preparation of chemical products on electrodes when a current is passed through solutions (the production of chlorine and alkaline , the production and purification of non-ferrous and rare metals, the electrosynthesis of organic compounds). An important sphere of practical application of electrolysis is the *electroplating* of metals

and the preparation of metal matrices. Another important field of engineering based on electrochemical processes is the creation of chemical sources of current (electrochemical or so-called galvanic cells, including accumulators) in which a chemical reaction is used as a source of electric current.

Electrochemical methods of chemical analysis such as electroanalysis, conductometry, potentiometry and polarography have been greatly developed, and their theory is also studied by electrochemistry.

The appearance of electrochemistry as a science is associated with the names of L. Galvani, A. Volta and V. Petrov, who on the border line between the 18th and 19th centuries discovered and investigated electrochemical (galvanic) cells. H. Davy and M. Faraday in the first decades of the 19th century studied electrolysis. The rapid development of electrochemistry at the end of the 19th century is due to the appearance of S. Arrhenius's theory of electrolytic dissociation (1887) and to the work of W. Nernst on the thermodynamics of electrode processes. Arrhenius's theory was further developed by P. Debye and E. Hückel (1923), who worked out the electrostatic theory.

Characteristic of the last few decades is the rapid development of electrochemical kinetics, investigation of the phenomena of overvoltage, corrosion, electroplating, etc.

**15.2. Two Kinds of Conductors.** Solid and liquid conductors, the passage of an electric current through which does not result in the transport of matter in the form of ions, are called *electronic conductors*. An electric current appears in them owing to the flow of electrons (*electronic conductivity*). These conductors include solid and liquid metals and certain non-metals (graphite, zinc and lead sulphides).

Substances, the passage of a current through which leads to transport of matter in the form of ions (*ionic conductivity*) and chemical transformations at the current inlet and outlet (electrochemical reactions), are called *electrolytic conductors*. Typical conductors of this kind are solutions of salts, acids and bases in water and some other solvents, molten salts and some solid salts. As a rule, in electrolytic conductors electricity is conducted by positive (cations) and negative (anions) ions, but certain solid salts are characterized by *unipolar* conductivity, i.e. the current is carried in them only by ions of one sign—cations (for example, in AgCl) or anions ($BaCl_2$,$ZrO_2$ + CaO, solutions of the alkali metals in liquid ammonia).

The classification of conductors depending on the type of conductivity (electronic or ionic) is a relative one. Solids are known with a mixed conductivity, for example the beta-modification of $Ag_2S$,

ZnO, $Cu_2O$, etc. A transition from ionic to mixed conductivity is observed in some salts (CuCl) when they are heated. A similar transition to mixed conductivity is observed in solutions of the alkali and alkali-earth metals in liquid ammonia when the concentration is increased.

Conductors of the second kind are called *electrolytes*. As indicated above, they may be pure substances or solutions. Frequently the term *electrolyte* is applied to a substance whose solutions conduct an electric current. These solutions are called electrolyte ones. We shall use the term *electrolyte* in the first sense, i.e. we shall apply this term to a substance (in the pure state or in a solution), the passage of a current through which is due to the motion of ions, and electrochemical reactions proceed on the electrodes immersed in it. These reactions usually (but not necessarily) result in decomposition of the solute (electrolysis).

**15.3. Electrochemical Reactions.** Electrochemical reactions proceed on the electrode (electronic conductor)-electrolyte interface. Their cause is the impossibility for electrons—the current carriers in the electrodes—to freely travel in the electrolyte. These reactions consist in the exchange of electrons between the electrode and the ions (molecules) in the solution. On the cathode the electrons pass from the electrode to the ions (or molecules), on the anode in the reverse direction, the ions (molecules) losing or changing their electric charge. This is a primary electrochemical reaction whose products quite frequently enter into further reactions not associated with the transport of the current by the ions. The following are examples of cathode reactions:

$$Cu^{2+} + 2e \longrightarrow Cu \tag{1}$$

$$Fe^{3+} + e \longrightarrow Fe^{2+} \tag{2}$$

$$2H_3O^+ + 2e \longrightarrow H_2\,(g) + 2H_2O \tag{3}$$

Reactions of the following type can proceed on the anode:

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e \tag{4}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e \tag{5}$$

$$2Cl^- \longrightarrow Cl_2(g) + 2e \tag{6}$$

$$Zn \longrightarrow Zn^{2+} + 2e \tag{7}$$

The material of the electrode may participate in an electrochemical reaction [reaction (7)], but it may also remain inert (the other reactions). In the latter case metals [reaction (1)] or gases [reactions (3), (4) and (6)] may be liberated on the surface of the electrode.

Finally, an electrochemical reaction may also proceed in the absence of the transition of ions from the solution to an electrode and vice versa. In these cases the current is transported only by electrons, but on the surface of the electrode in the solution the ions change their valence [reactions (2) and (5)]. A complex of two electrochemical reactions of which one proceeds on the cathode and the other on the anode gives a chemical reaction of electrolysis or a reaction proceeding in an electrochemical cell:

$$Cu^{2+} + 2Cl^- \longrightarrow Cu\,(s) + Cl_2 \qquad (1)+(6)$$

$$2H_3O^+ + 2OH^- \longrightarrow \frac{1}{2}\,O_2 + H_2 + 3H_2O \qquad (3)+{}^1/_2(4)$$

or

$$H_2O \longrightarrow \frac{1}{2}\,O_2 + H_2$$

**15.4. Laws of Electrolysis (Faraday's Laws).** After a study of various types of electrolytic reactions, Faraday (1833) discovered two simple and fundamental laws of behaviour, now called *Faraday's laws of electrolysis.*

The first law states that *the amounts of substances transformed in electrolysis are proportional to the quantity of electricity passed through the electrolyte.*

The second law states that *when the same quantity of electricity passes through different electrolytes, the amounts of the different substances transformed at the electrodes (liberation from the solution, a change in valence) are proportional to the chemical equivalents of these substances.*

The passage of one coulomb of electricity through solutions of $AgNO_3$, $CuSO_4$ and $H_2SO_4$ liberates 1.118 mg of silver, 0.3293 mg of copper and 0.010446 mg of hydrogen, respectively. These quantities are called *electrochemical equivalents*; they are directly proportional to the chemical equivalents. Indeed, expressing the above values in grammes and comparing them with the values of the gramme-equivalents, we get

$$107.870/1.1180 \times 10^{-3} = 96\,484$$

$$31.77/3.293 \times 10^{-4} = 96\,481$$

$$1.007\,97/1.0446 \times 10^{-5} = 96\,494$$

For the liberation or transformation of one gramme-equivalent of any substance with the aid of a current, it is always necessary to use the same quantity of electricity, called the *Faraday constant* (or the *faraday*). The accurately measured value of the Faraday constant is $F = 96\,487.0 \pm 1.6$ C/g-equiv. This is the charge carried by one gramme-equivalent of ions of any species. Multiplying this

number by $z$ (the number of elementary charges of an ion), we get the quantity of electricity carried by one gramme-ion. Dividing the Faraday constant by the Avogadro constant, we get the charge of one single-valent ion equal to the charge of an electron:

$$e = \frac{96\,487.0}{6.0225 \times 10^{23}} = 1.6021 \times 10^{-19}\ \mathrm{C} = 4.8030 \times 10^{-10}\ \mathrm{cgs}_Q$$

Faraday's laws are strictly obeyed for electrolytic conductors. The observed deviations from these laws are apparent ones. They are often due to the existence of parallel electrochemical reactions not taken into account. For example, in the electrolysis of a solution of NaCl the amounts of NaOH and $Cl_2$ formed are less than those calculated according to Faraday's law owing to the partial formation of the ions $ClO^-$, $ClO_3^-$, etc. Deviations from Faraday's law in industrial installations are due to current leakage, the losses of a substance upon splashing of the solution, etc.

In industrial installations the ratio between the amount of the product obtained in electrolysis to the amount computed according to Faraday's law is less than unity and is called the *current efficiency*.

In carefully prepared laboratory measurements for single electrochemical reactions the current efficiency is equal to unity (within the limits of the errors of the experiment). Faraday's law is exact, and for this reason it forms the basis of the most accurate method of measuring the quantity of electricity passing through a circuit according to the amount of substance liberated on an electrode. For such measurements use is made of a silver, copper, iodine or gas *coulometer* (*coulometry*).

**15.5. Electrical Units.** The intensity of a direct current $I$, the potential difference $U$ and the resistance $R$ are related by Ohm's law

$$I = \frac{U}{R} \tag{15.1}$$

The basic electrical unit in the SI system is the *ampere* (A)—the intensity of an unchanging current which, upon flowing along two parallel conductors of infinite length and with a negligibly small round section, arranged at a distance of one metre from each other in a vacuum, would induce between these conductors a force equal to $2 \times 10^{-7}$ newtons per metre of length. The ampere is also a practical unit for measuring current intensity ($1\ \mathrm{A} = 3 \times 10^9\ \mathrm{cgs}_I$).

The unit of electrical potential in the SI system and the practical unit for measuring potential is the *volt* (V)—the potential difference between two points of an electric field for which a work equal to one joule is required to move a charge of one coulomb between them ($1\ \mathrm{V} = 3.34 \times 10^{-3}\ \mathrm{cgs}_u$).

The unit of electrical resistance in the SI system and also the practical unit of resistance is the *ohm* (Ω)—the resistance of a conductor

in which a current of one ampere flows with a potential difference of one volt across its ends ($1\ \Omega = 1.11 \times 10^{-12}\ cgs_R$)[1].

Ohm's law, which serves as the basis for determining the unit of electrical resistance, can be applied to a system of conductors including electrolytes if we take into account (and deduct) the potential jumps at the electrode-solution and solution-electrode phase interfaces. Deviations from Ohm's law in electrolytes are observed for electrolytes in high-frequency fields or at very great field intensities.

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[1] The units defined above—the ampere, volt and ohm—are also called *absolute units* (absolute ampere, volt and ohm). They differ slightly from the practical *international units* that were in general use until recently (in the USSR up to 1948) and were completely discarded. The values of the international units were as follows:

1 international ampere = 0.999 85 abs. ampere
1 international volt = 1.000 35 abs. volt
1 international ohm = 1.000 500 abs. ohm.

# CHAPTER 16

# THEORY OF ELECTROLYTES

**16.1. Fundamentals of Theory of Electrolytic Dissociation.** For electrolytes the lowering of the freezing point and the osmotic pressure are considerably greater than the relevant quantities for nonelectrolytes [see Vol. 1, Eqs. (7.25) and (7.31)]. J. van't Hoff (1886) introduced the empirical coefficient $i > 1$, whose physical meaning will be explained below, into the equation for the osmotic pressure $\Pi$

$$\Pi = icRT \tag{16.1}$$

The theory of electrolytic dissociation was proposed by S. Arrhenius (beginning from 1884), who further developed certain ideas put forward earlier by a number of scientists (R. Clausius, C. Williams, and others).

Salts, acids and bases partly or completely decompose (dissociate) into ions when dissolved in water or certain other polar solvents. These ions are present in a solution regardless of whether an electric current passes through the solution or not. As a result the number of independently moving solute particles is greater than in the absence of dissociation. The lowering of the freezing point, the osmotic pressure and the values of other colligative properties of solutions (see Vol. 1, p. 237) grow in direct proportion to the number of particles. With a reduction in concentration the dissociation into ions (electrolytic dissociation), in accordance with the law of mass action, approaches the limiting value, i.e. becomes practically complete.

Applying the law of mass action to any reversible reaction of electrolytic dissociation

$$\begin{array}{ccccc} K_{\nu_+}A_{\nu_-} & \rightleftarrows & \nu_+K^{z+} & + & \nu_-A^{z-} \\ 1-\alpha & & \nu_+\alpha & & \nu_-\alpha \end{array} \tag{16.2}$$

we obtain for equilibrium

$$K_d = \frac{m_+^{\nu_+} m_-^{\nu_-}}{m(K_{\nu_+} A_{\nu_-})} \tag{16.3}$$

where $K_d$ = constant of electrolytic dissociation
$m$ = molality of ions and undissociated molecules.

It is evident that $\nu_+ z_+ = \nu_- z_-$.

We can also use the molar-volume concentrations $c$, but in this case the dissociation constant will have a different numerical value. Let us introduce as a measure of electrolytic dissociation the degree of dissociation $\alpha$ determined as the fraction of molecules decomposing into ions (cf. Vol. 1, Sec. 8.5). Hence the amounts of gramme-ions formed upon the dissociation of one mole of a dissociating substance will be expressed by the quantities written under the chemical formulas in Eq. (16.2), and the equation for the dissociation constant will become

$$K_d = \frac{m_0^{\nu_+ + \nu_- - 1} \alpha^{\nu_+ + \nu_-}}{1 - \alpha} \tag{16.4}$$

where $m_0$ is the molality of the solution when calculated for the completely undissociated substance.

In the particular case when $\nu_+ = \nu_- = 1$ we have

$$K_d = \frac{m_0 \alpha^2}{1 - \alpha} \tag{16.5}$$

It is obvious that the sum $\nu_+ + \nu_-$ in Eq. (16.4) is equal to the total number of ions formed when one molecule dissociates. Denoting this sum by $\nu$, from Eq. (16.2) we find the average total number of particles (ions and molecules) formed upon the electrolytic dissociation of one molecule which is obviously equal to the van't Hoff coefficient $i$:

$$i = 1 + (\nu_+ + \nu_- - 1)\alpha = 1 + (\nu - 1)\alpha \tag{16.6}$$

Having found the van't Hoff coefficient $i$, we can obviously compute the degree of dissociation $\alpha$ by Eq. (16.6). Here the coefficients of Eq. (16.2) must be known. As the dilution grows, the van't Hoff coefficient approaches an integer (2, 3, 4, depending on the number of ions formed upon the solution of a molecule of the substance[1]):

[1] It is a general knowledge that ions do not exist in an aqueous solution in the free state; they are hydrated (solvated). The equations of electrolytic dissociation do not take this into account. It would be more correct in principle to compile the equations of dissociation with account taken of solvation, but in the absence of accurate data on solvation this gives practically nothing, and for this reason for simplicity we shall also conventionally write equations for electrolytic dissociation and for ionic reactions in solutions without taking into consideration the solvation of the ions (except for the hydrogen ion—hydroxonit in $H_3O^+$). However, one must always remember the existence of solvation and its important role.

$$NaCl \rightleftharpoons Na^+ + Cl^- \qquad i \longrightarrow 2$$

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-} \qquad i \longrightarrow 3$$

$$LaCl_3 \rightleftharpoons La^{3+} + 3Cl^- \qquad i \longrightarrow 4$$

$$K_4Fe(CN)_6 \rightleftharpoons 4K^+ + Fe(CN)_6^{4-} \qquad i \longrightarrow 5$$

These are the fundamentals of the theory of electrolytic dissociation proposed by Arrhenius. This theory was first met by most chemists (including D. Mendeleev) with disapproval. They considered that such active substances as free chlorine and sodium cannot exist in water. These objections, however, were connected with the improper transfer of the properties of elements to ions, which at that time were for scientists an unusual form of existence of matter. These objections soon disappeared, but subsequently other shortcomings of Arrhenius's original theory came to light, which later (1912-1925) made it necessary to appreciably reconsider the theory of electrolytes. The points of departure of the original theory, however, still remain true at present.

**16.2. Causes of Electrolytic Dissociation.** Solids that form electrolytic solutions when dissolved in water or other polar solvents are, as a rule, crystalline bodies having ionic lattices or lattices similar to them. Molecules of a substance do not exist in purely ionic lattices, and a crystal of any size can be considered as one huge molecule. The ions of opposite signs forming such a lattice are bound to one another by great electrostatic forces. When the ions pass into solution, the energy of interaction of the ions with the dipole molecules of the solvent which pulls the lattice ions into the solution is opposed to the energy of electrostatic interaction of the ions in the lattice. The ions are surrounded by molecules of the solvent, which form a solvation (in a particular case a hydration) shell around each ion. The energy of interaction of ions of different signs that have passed into the solution and are surrounded by solvation shells diminishes in comparison with the energy of their interaction in the lattice (with equal distances $r$ between the ions) inversely proportional to the relative permittivity of the solvent $\varepsilon_r$ in accordance with Coulomb's law[1]

$$E = -\frac{z_1 z_2 e^2}{\varepsilon_r r}$$

[1] Coulomb's law is applicable with any distances between point charges in a vacuum. The notion of point charges is permissible when the distances between the ions are great. At high concentrations the distances between ions are small and account must be taken of the distribution of the charges inside an ion. In addition since the relative permittivity $\varepsilon_r$ is a statistically mean macroscopic characteristic of the electrical properties of a dielectric, it does not accurately reflect them if the space between neighbouring ions is small and is filled with a small amount of solvent molecules. For this reason the form of Coulomb's law given here is not entirely accurate when applied to concentrated electrolytes.

where $z_1$ and $z_2$ = number of elementary charges of a cation and anion

$r$ = distance between a cation and an anion.

If the energy of interaction of the ions with the solvent becomes commensurable with the energy of ions vibrating about the state of equilibrium in a crystal lattice, solution accompanied by dissociation occurs. It should be remembered that in dissolving, the Gibbs energy $G$ of the system should decrease, while the internal energy (and enthalpy) may either decrease or increase (a negative or a positive heat of solution). The changes in the energy in the hydration of free gaseous ions are great negative quantities (see Vol. 1, p. 66, Fig. 2.2). The energy of interaction of ions with the solvent (the energy of solvation) will be considered in Sec. 16.9.

Interaction of dipole molecules of the solvent with elements of a crystal lattice may lead to the formation of an electrolyte even upon the solution of substances having a molecular lattice, a lattice of an intermediate type or that are in the gaseous state (the atoms in the gas molecules are bound covalently).

Arrhenius's theory appeared on the basis of van't Hoff's theory of dilute solutions, which considers solutions as ideal gases, and was a development of the latter.

It is clear from what has been said above that the determining part in electrolytic dissociation is played by the interaction of the ions with the solvent (hydration in aqueous solutions, solvation in the general case). The great significance of the hydration of ions was first indicated by V. Kistyakovsky (1888-1890) and I. Kablukov (1891). They laid the foundation for the development of the theory of electrolytes in the direction indicated by Mendeleev, i.e. combined the so-called solvation theory and the physical theory of van't Hoff and Arrhenius[1].

The relation between the relative permittivity $\varepsilon_r$ of a solvent and its ability to form solutions conducting an electric current was noted long ago. Water ($\varepsilon_r$ = 81 at 18 °C), and also HCN ($\varepsilon_r$ = 107 at 25 °C) and HCOOH ($\varepsilon_r$ = 57.0 at 25 °C) belong to solvents causing great dissociation. The lower alcohols and ketones, acetic acid and pyridine have relative permittivities ranging from 20 to 35 and are also capable of forming electrolytic solutions, although to a smaller extent than water.

In addition to the value of the relative permittivity, of great significance is a more direct interaction of the solvent molecules with those of the solute. This interaction often leads to the formation of new molecules or molecular complexes which are capable of dissociating into ions in the given solvent.

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[1] For Mendeleev's vie· s on solutions see Vol. 1, Sec. 5.4.

As indicated above, when substances with ionic and strongly polar lattices are dissolved, no new ions form, since they already exist in the lattice. In these cases the solvent only divides oppositely charged ions and separates them from one another. This process appreciably differs from ionization in gases, where collision of the gas molecules with rapidly moving particles causes an electron to be knocked out of a molecule, the result being the formation of a positively charged ion. Hence the term *electrolytic dissociation*, as applied to the process of solution of ionic crystals in polar solvents considered above, characterizes this process as the decomposition of the crystalline substance into ions. The latter move independently in the solution and form a solution conducting current, i.e. an electrolyte. The term *ionization* is less correct, since this process has nothing in common with ionization in gases. It should be remembered that electrolytic dissociation is the result of the action of polar molecules of the solvent on an ionic crystal (or on a non-polar molecule). For this reason the ions formed inevitably enter into close interaction with the solvent molecules (solvation), and in this sense are far from being free.

**16.3. Shortcomings of Arrhenius's Theory.** The space distribution of the ions in a solution is very important for the theory of electrolytes. According to the original theory of electrolytic dissociation based on van't Hoff's physical theory of solutions, ions in a solution are in a state of chaotic motion, consequently in a state similar to that in an ideal gas. The possibility of applying laws for the gaseous state to electrolytes was explained by this circumstance.

The notions of the chaotic distribution of ions in a solution, however, do not correspond to the actual conditions, since the electrostatic interaction between the ions is ignored. Electrical forces act over relatively great distances. In strong electrolytes, where dissociation is great, the concentration of the ions is high and the distances between them are small, the electrostatic interaction between the ions is so great that it cannot fail to affect the nature of their distribution. A tendency of orderly distribution appears, the latter being to a certain extent similar to the distribution of ions in ionic crystals, where each ion is surrounded by ions of an opposite sign.

Thus, the distribution of the ions is determined by the ratio between the electrostatic energy and the energy of the chaotic motion of the ions. These energies are comparable in value, hence the actual distribution of the ions in an electrolyte is intermediate between chaotic and orderly distribution. This forms the peculiar and specific nature of electrolytes and leads to the difficulties appearing in developing a theory of electrolytes, since it is first of all essential to determine the nature of ion distribution.

The electrostatic forces tend to create such a distribution when every ion is surrounded only by ions of the opposite sign. But this is counteracted by the chaotic motion of the ions leading to their random distribution. These opposite tendencies lead to the formation of a specific ionic atmosphere around each ion in which ions of the opposite sign (in comparison with the central one) predominate.

Arrhenius's theory did not take this circumstance into account,

and many conclusions of this theory were in contradiction with the results of experiments. Arrhenius assumed that the interaction of ions in a solution does not affect their distribution and motion, which remain chaotic as in mixtures of ideal gases. On these grounds he stated that the properties of separate ions in a solution do not depend on the concentration, and that some properties of a solution as a whole are proportional to the number of ions (or to the total number of solute particles). Thus according to Arrhenius the electrical conductivity of a solution should be proportional to the number of ions and can serve as a measure of the degree of dissociation.

With considerable concentrations of the ions, however, their electrostatic interaction, as already indicated should result in their mutual attraction (i.e. in a reduction in the freedom of their motion). Thus, the velocity of the ions in an electrical field at a given potential difference will decrease with an increase in the concentration owing to the mutual attraction of ions with opposite signs. This attraction acts like additional friction, and for this reason the electrical conductivity by itself cannot serve as an unambiguous measure of the degree of dissociation. For greatly dissociating electrolytes, especially at high concentrations, the error will be quite significant.

According to Arrhenius's classical theory, when $m = 0.01$ to $0.1$ the degree of dissociation of strong electrolytes $\alpha = 0.75$ to $0.95$. The dissociation constants calculated from these values sharply change with the concentration, i.e. they are not constants. The degree of dissociation calculated according to the electrical conductivity differs noticeably from that found for concentrated electrolytes by Eq. (16.6). Other facts also indicate that the degree of dissociation of strong electrolytes is considerably higher than that calculated according to Arrhenius's theory. Thus, the catalytic action of hydroxonium ions ($H_3O^+$) in strong electrolytes changes in proportion to the total concentration of the solute, which points to the independence of the degree of dissociation on the concentration.

The absorption spectra of combined dispersion (Raman spectra) of the solutions of salts, even concentrated ones, have no lines and bands that could be ascribed to undissociated molecules, although the concentration of the latter, according to the law of mass action, should be sufficient for them to be detected. Many other properties of dilute solutions of strong electrolytes, for example the heat capacity, refraction and heat of reaction, can be more or less accurately calculated as additive ones on the basis of the relevant quantities for the ions and solvent without taking into account the undissociated molecules.

These facts obviously contradict the tenets of the classical theory of electrolytic dissociation which, therefore, is applicable only to weak electrolytes. Equation (16.5) with corrections limiting the

dependence of $\alpha$ on the activities of the ions may be applied to them. Weak electrolytes are ones for which $\alpha \leqslant 0.05$.

The weak points of Arrhenius's theory made scientists search for new groundstones of the theory of strong electrolytes. In 1894 J. van Laar pointed to the necessity of taking into consideration the electrostatic forces in an electrolyte. W. Sutherland (1902), A. Hantzsh (1906) and N. Bjerrum (1906) advanced the hypothesis of the complete dissociation (ionization) of strong electrolytes. Later N. Bjerrum, S. Milner (1912) and J. Ghosch (1918) attempted to create a new theory of strong electrolytes on the basis of this hypothesis, but without much success. The foundation of the electrostatic theory of electrolytes was laid somewhat later (1923) in the works of P. Debye and E. Hückel.

**16.4. Activity and Activity Coefficient of Electrolytes.** The activity $a_2$ of a dissolved salt can be determined according to the vapour pressure, freezing point, and according to data on its solubility. It is calculated in the same ways that are set out briefly in Vol. 1 (Chaps. 6 and 7). A specific and the most convenient method of determining the activities and activity coefficients of electrolytes is the method of e.m.f.s (electromotive forces). All the methods of determining the activity of a salt and the equations mentioned above lead to a quantity characterizing the real thermodynamic properties of the dissolved salt as a whole, regardless of whether or not it is dissociated. In the general case, however, the properties of different ions are not the same, and in principle it is possible to introduce and consider thermodynamic functions separately for ions of different species. For this purpose the practical activity coefficient $\gamma'$ is used [see Vol. 1, Sec. 6.8, Eqs. (6.24) and (6.31b)]:

$$\left.\begin{aligned} \mu_+ &= \mu_+^\circ + RT \ln a_+ = \mu_+^\circ + RT \ln m_+ + RT \ln \gamma_+' \\ \mu_- &= \mu_-^\circ + RT \ln a_- = \mu_-^\circ + RT \ln m_- + RT \ln \gamma_-' \end{aligned}\right\} \qquad (16.7)$$

where $\gamma_+'$ and $\gamma_-'$ are the activity coefficients at concentrations equal to the molality $m$, i.e. the so-called practical activity coefficients[1].

But the thermodynamic properties of various ions cannot be determined separately from experimental data without additional assumptions. In using any methods, the measured changes in the thermodynamic properties always relate to a great number of particles, in the given case to ions, namely, to all the ions forming the given substance. All that we can do is measure only the mean thermodynamic quantities for the ions into which a molecule of this substance decomposes.

Let us find by Eq. (16.7) the relation between the mean values of the chemical potential and the activity for a salt and the values of the potentials and the activity for ions of various species. Let the

[1] For the use of different measures of concentration and the relations between the activity coefficients corresponding to these measures see Vol. 1, Sec. 6.8, pp. 203-206.

electrolytic dissociation of a salt proceed according to the equation

$$A_{\nu_+}B_{\nu_-} = \nu_+A^{z_1+} + \nu_-B^{z_2-}$$

where $\nu_+$ and $\nu_-$ = numbers of cations and anions
$z_1$ and $z_2$ = their charge numbers.

The changes in the chemical potentials of the components of a solution with a change in its composition and at a constant pressure and temperature are related by the Gibbs-Duhem equation [see Vol. 1, p. 167, Eq. (5.12)]. Let us use the assumption made above on the complete dissociation of strong electrolytes. In the following we shall be able to apply the derived relations to weak electrolytes with account taken of the incomplete dissociation of the latter.

We can consider that a solution of one salt consists of two substances—a solvent (1) and a dissolved salt (2) and write

$$n_1\, d\mu_1 + n_2\, d\mu_2 = 0 \qquad \text{(a)}$$

$$n_1\, d \ln a_1 + n_2\, d \ln a_2 = 0 \qquad \text{(b)}$$

where $n_1$ and $n_2$ are the numbers of moles of the components, i.e. of the solvent and solute, respectively.

If we take 1000 g of the solvent, then $n_1 = 1000/M_1$ and $n_2 = m$ is the molality. Hence Eq. (a) becomes

$$\frac{1000}{M_1} d \ln a_1 + m d \ln a_2 = 0 \qquad (16.8)$$

Considering, on the other hand, that the solution consists of a solvent, cations and anions, for a solution in 1000 g of the solvent we get

$$\left.\begin{aligned} &\frac{1000}{M_1} d\mu_1 + m_+ d\mu_+ + m_- d\mu_- = 0 \\ \text{or} \quad & \\ &\frac{1000}{M_1} d \ln a_1 + m_+ d \ln a_+ + m_- d \ln a_- = 0 \end{aligned}\right\} \qquad (16.9)$$

The change in the value of $\mu_1$ (for the solvent) does not depend on whether we consider the salt as one constituent of the solution or consider the cations and anions as separate constituents. This is obvious, for instance, from the equation

$$\Delta\mu_1 = RT \ln p_1/p_1^\circ$$

similar to Eq. (6.3) (see Vol. 1, p. 180), where $p_1$ depends on the concentration of the solution (according to experiments), but not on how we consider the solute. Therefore the first terms in Eqs. (16.8) and (16.9) are equal. After subtracting Eq. (16.8) from Eq. (16.9) we get

$$m_+\, d \ln a_+ + m_-\, d \ln a_- - m d \ln a_2 = 0 \qquad (16.10)$$

It can be seen from the equation of dissociation of the salt that upon complete dissociation

$$m_+ = \nu_+ m \text{ and } m_- = \nu_- m \qquad (16.11)$$

Inserting expression (16.11) into Eq. (16.10), we get

$$\nu_+ \, d \ln a_+ + \nu_- \, d \ln a_- - d \ln a_2 = 0$$

or

$$d \ln \frac{a_+^{\nu_+} a_-^{\nu_-}}{a_2} = 0$$

$$\frac{a_+^{\nu_+} a_-^{\nu_-}}{a_2} = \text{const} \tag{16.12}$$

The standard states for finding the values of the activities are determined as follows:

$$\left.\begin{array}{l} \lim a_+ \to m_+ = \nu_+ m \\ \lim a_- \to m_- = \nu_- m \end{array}\right| \quad \text{when } m \to 0 \tag{16.12a}$$

The activity $a_2$ of the dissolved salt as a component of the solution can be determined by Eq. (16.8) without considering its dissociation. The standard state for the activity $a_2$ is so selected that the constant in Eq. (16.12) is equal to unity. Hence

$$a_+^{\nu_+} a_-^{\nu_-} = a_2 \tag{16.13}$$

Since no methods exist for experimentally determining the values of $a_+$ and $a_-$ separately, the mean ionic activity $a_\pm$ is introduced, which is determined as follows:

$$a_\pm \equiv (a_+^{\nu_+} a_-^{\nu_-})^{1/\nu} \tag{16.14}$$

Here $\nu = \nu_+ + \nu_-$, and from Eqs (16.13) and (16.14) we have

$$a_\pm^{\nu} = a_2 \tag{16.15}$$

Thus we have two quantities characterizing the activity of a dissolved salt. The first of them is the *molar activity*, i.e. the activity of a salt determined independently of dissociation, which is found by the same experimental methods and by the same equations as the activity of the components in non-electrolytes. The second quantity is the *mean ionic activity* $a_\pm$. Both quantities are related by Eq. (16.15).

In the following we shall mainly use the mean ionic activity $a_\pm$. Cryoscopy and a method based on determining the vapour pressure make it possible to find the value of $a_2$, and the value of $a_\pm$ is found by Eq. (16.15).

Let us now introduce the *activity coefficients of ions* $\gamma'_+$ and $\gamma'_-$, the *mean ionic molality* $m_\pm$ and the *mean ionic activity coefficient* $\gamma'_\pm$, namely,

$$a_+ = \gamma'_+ m_+; \quad a_- = \gamma'_- m_- \text{ and } m_\pm = (m_+^{\nu_+} m_-^{\nu_-})^{1/\nu} = (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} m \tag{16.16}$$

Substitution for $a_+$ and $a_-$ in Eq. (16.14) of their expressions from Eq. (16.16) and use of condition (16.12a) yield

$$a_\pm \equiv (\gamma_+'^{\nu_+}\gamma_-'^{\nu_-})^{1/\nu}(\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu} m \equiv \gamma_\pm' m_\pm \tag{16.17}$$

Obviously

$$\gamma_\pm' = (\gamma_+'^{\nu_+}\gamma_-'^{\nu_-})^{1/\nu} \tag{16.17a}$$

The quantity $\gamma_\pm'$ is an important characteristic of the deviation of a salt solution from the ideal state.

The basic quantities are thus related as follows:

$$a_\pm = \gamma_\pm' m_\pm = \gamma_\pm'(\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu} m = L\gamma_\pm' m \tag{16.18}$$

where $L = (\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}$ is a constant quantity for salts of each definite type of valence.

The following activities and activity coefficients can be used for electrolytic solutions, as for non-electrolytic ones [see Vol. 1, pp. 203-205, Eqs. (6.31) to (6.33)]:

$$\gamma_\pm = \frac{a_{\pm x}}{x_\pm} = \text{rational activity coefficient (not used practically)}$$

$$\gamma_\pm' = \frac{a_{\pm m}}{m_\pm} = \text{practical activity coefficient (mean molal)}$$

$$f_\pm = \frac{a_{\pm c}}{c_\pm} = \text{mean molar activity coefficient.}$$

The last two coefficients are related as follows:

$$\ln \gamma_\pm' = \ln f_\pm + \ln\left(\frac{\rho}{\rho_0} - \frac{cM_2}{1000\rho_0}\right)$$

$$\ln f_\pm = \ln \gamma_\pm' + \ln \frac{\rho_0[M_1 + (M_2 - M_1)x]}{\rho M_1(1-x)}$$

where $M_1$ and $M_2$ = molecular masses
$\nu$ = number of ions formed by the dissociation of a molecule
$\rho$ and $\rho_0$ = densities of solution and solvent, respectively.

The differences between $\gamma_\pm$, $\gamma_\pm'$ and $f_\pm$ acquire a noticeable significance in studying solutions in various solvents, including mixed ones, where $\rho$ and $M_1$ are variables.

Table 16.1 gives the numerical values of the quantity $L$ for salts dissociating into ions having different valences.

The main methods of measuring the value of $\gamma_\pm$ and $\gamma_\pm'$ are the cryoscopic one (see Vol. 1, Sec. 7.8) and the method of e.m.f.s, which will be described in Sec. 22.1.

Numerous investigations (especially of the school of G. Lewis) showed that the curve of the dependence of the mean ionic activity

TABLE 16.1
**Values of $L$ [see Eq. (16.18)] for Salts of Various Valence Kinds**

| Valence kind (valences of cation and anion) | Salt | $\nu_{\pm}$ | $L=\left(\nu_+^{\nu_+}\nu_-^{\nu_-}\right)^{1/\nu}$ |
|---|---|---|---|
| 1-1; 2-2; 3-3 | $KCl$, $ZnSO_4$, $LaFe(CN)_6$ | $(\nu_+\nu_-)^{1/2}$ | 1 |
| 2-1 | $CaCl_2$ | $(\nu_+\nu_-^2)^{1/3}$ | 1.588 |
| 1-2 | $Na_2SO_4$ | $(\nu_+^2\nu_-)^{1/3}$ | 1.588 |
| 3-1 | $LaCl_3$ | $(\nu_+\nu_-^3)^{1/4}$ | 2.279 |
| 1-3 | $K_3Fe(CN)_6$ | $(\nu_+^3\nu_-)^{1/4}$ | 2.279 |
| 4-1 | $Th(NO_3)_4$ | $(\nu_+\nu_-^4)^{1/5}$ | 3.031 |
| 1-4 | $K_4Fe(CN)_6$ | $(\nu_+^4\nu_-)^{1/5}$ | 3.031 |
| 3-2 | $Al_2(SO_4)_3$ | $(\nu_+^2\nu_-^3)^{1/5}$ | 2.561 |

coefficient on the concentration of a solution (molality) has a minimum. If we depict this dependence in the coordinates log $\gamma'_{\pm}$ versus

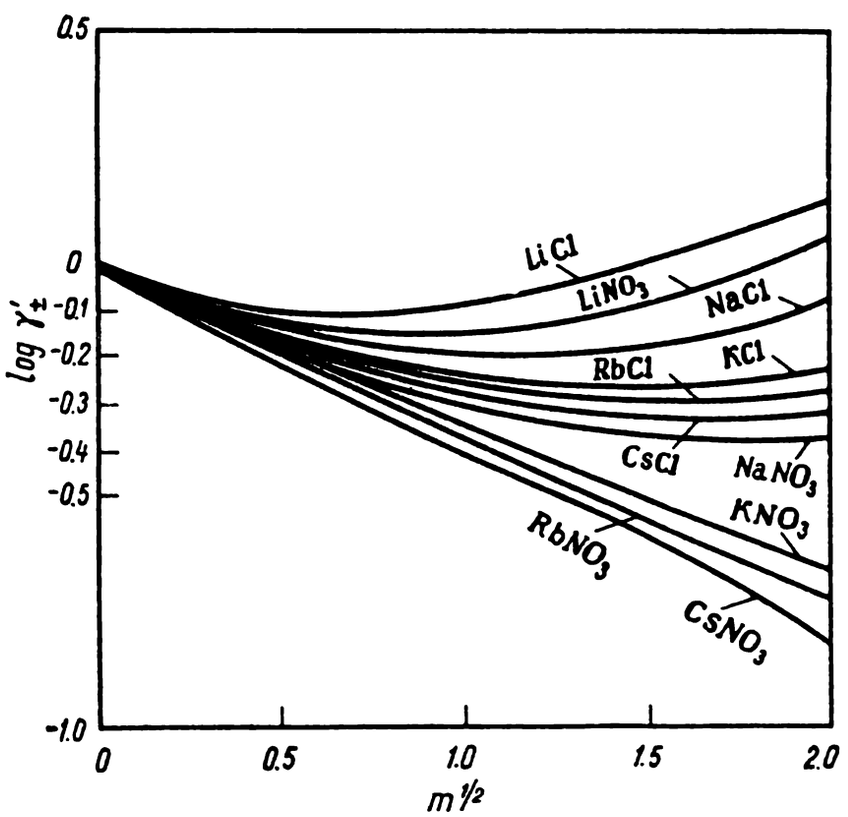


**Fig. 16.1.** Mean activity coefficients for mono-monovalent electrolytes at 25 °C

$m^{1/2}$, the dependence will be a linear one for dilute solutions. The slope of the straight lines corresponding to infinite dilution (the limiting lines) is the same for salts of one valence type (mono-monovalent, bi-monovalent salts, etc. see Figs. 16.1 and 16.2). The pre-

sence of other salts in a solution changes the activity coefficient of a given salt and displaces it to the right along a curve of the type shown in Fig. 16.1 or Fig. 16.2. The greater the charge of the ions of the added salt, the more do they influence the value of $\gamma'_{\pm}$ of the other salt. The summary influence of a mixture of salts in a solution on the activity coefficient of each of them is covered by a general

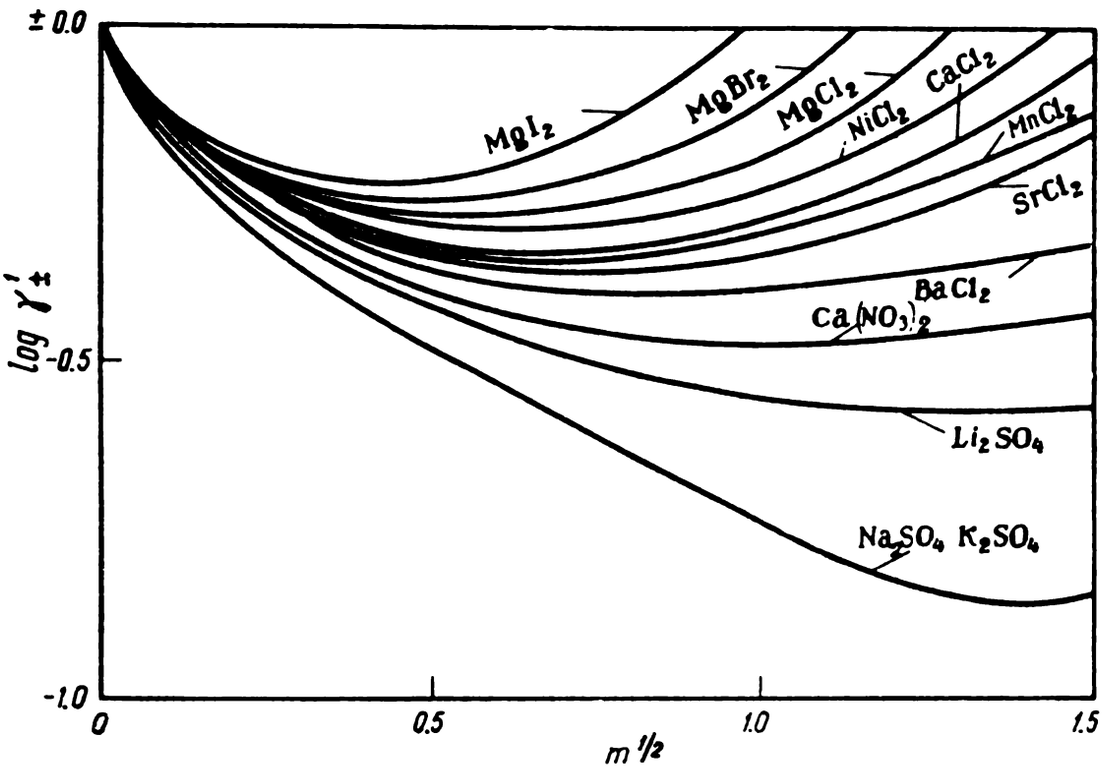


Fig. 16.2. Mean activity coefficients for 1-2- and 2-1-valent electrolytes at 25 °C

law, if the total concentration of all the salts in the solution is expressed through the *ionic strength*. The ionic strength of a solution is the half-sum of the products of the concentration of each ion and the square of its charge number $z$ (valence) taken for all the ions of the given solution.

If we use the molality as a measure of concentration, the ionic strength $I$ of a solution is determined by the expression

$$I = \frac{1}{2} \sum_i m_i z_i^2 \tag{16.19}$$

Here $i$ denotes the subscripts of all the ions of salts in the solution.

Since for each ion $m_i = \nu_i m_k$ (where $m_k$ is the molality of a salt), then for a given salt we have

$$m_+ z_+^2 + m_- z_-^2 = (\nu_+ z_+^2 + \nu_- z_-^2)\, m_k = 2 s_k m_k$$

and the sum $I$ includes the molality of each salt $m_k$ multiplied by the factor $s_k = \frac{1}{2}(\nu_+ z_+^2 + \nu_- z_-^2)$, which is constant for dissociating substances of the given valence kind. It is therefore more convenient to compute the ionic strength determined by Eq. (16.19) by the

equation

$$I = \frac{1}{2} \sum_k 2s_k m_k = \sum_k s_k m_k$$

The values of the factor $s_k$ for salts of various valence kinds are given in Table 16.2.

TABLE 16.2

**Values of Factor $s_k$ for Salts of Various Valence Kinds**

| Valence kind of salt | Salt | $s_k$ |
|---|---|---|
| 1-1 | NaCl | 1 |
| 2-2 | $ZnSO_4$ | 4 |
| 3-3 | $LaFe(CN)_6$ | 9 |
| 1-2; 2-1 | $Na_2SO_4$; $BaCl_2$ | 3 |
| 3-1; 1-3 | $LaCl_3$; $K_3Fe(CN)_6$ | 6 |
| 4-1; 1-4 | $Th(NO_3)_4$; $K_4Fe(CN)_6$ | 10 |
| 3-2 | $La_2(SO_4)_3$ | 15 |

G. Lewis and M. Randall discovered an *empirical law of ionic strength*[1], according to which the mean ionic activity coefficient $\gamma'_\pm$ for a substance dissociating into ions is a universal function of the ionic strength $I$ of the solution, i.e. in a solution with a given ionic strength all the substances dissociating into ions have activity coefficients that do not depend on the nature and concentration of the given substance, but depend on the number and valence of its ions.

This law is accurate only for very low concentrations ($m \leqslant 0.02$), at moderate concentrations it holds only approximately.

Figure 16.3 shows the quantity $\log \gamma'_\pm$ for hydrochloric and hydrobromic acids in solutions of alkali metal halides. For mono-monovalent electrolytes $s = 1$ and $I = \sum_k m_k$, and Fig. 16.3 gives the values of $\log \gamma_\pm$ as a function of the square root of the total molality of the relevant solution. A glance at the figure shows that the relation $\log \gamma'_\pm = f(m^{1/2})$ is approximately linear at low values of $m$ and does not depend on the nature of the salt within the confines of the given valence kind. It is clear from what has been said above that the law of ionic strength, at low summary concentrations, reflects the summary interaction of the ions of a solution with account of their valence.

[1] A theoretical substantiation of the law of ionic strength will be given below (Sec. 16.7).

**16.5. Statistical Theory of Electrolytes (Debye-Hückel Theory). Potential of Ionic Atmosphere.** The statistical theory of electrolytes is based on the following initial postulate: *ions are distributed in a solution (at each given moment) not randomly, but in accordance with the law of their Coulombian interaction.* On these grounds the distribution of ions of different signs around every individual ion has been found by the method of statistical physics. Thus, the existence of an *ionic atmosphere* (*ionic cloud*) around every ion was discovered. It was found to consist of ions of the opposite sign (to that of the

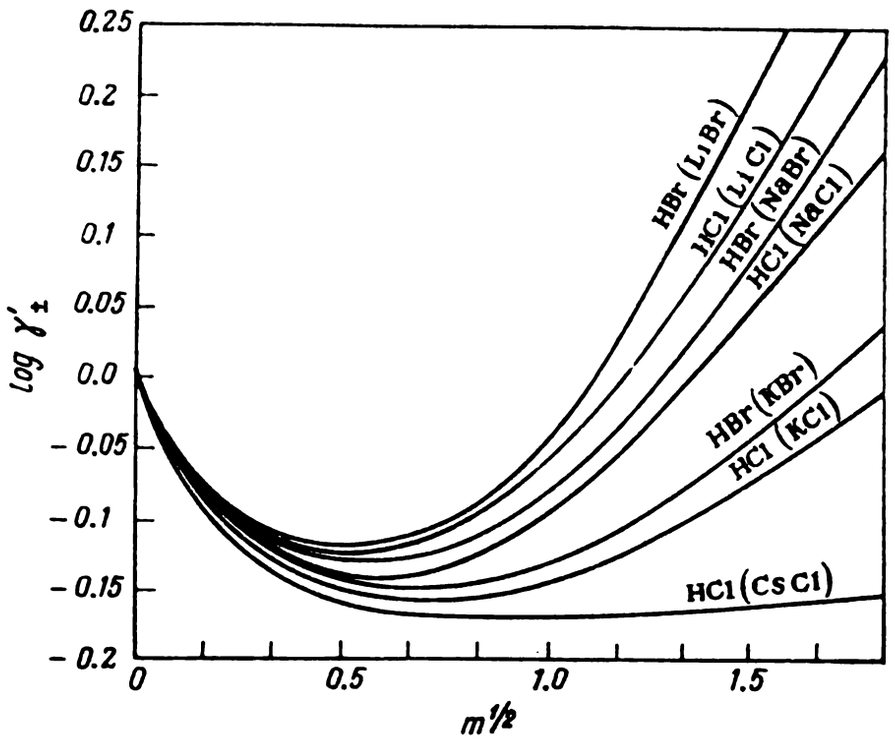


Fig. 16.3. Mean activity coefficients for hydrochloric and hydrobromic acids in solutions of alkali metal halides at 25 °C

central one). This statistically uneven distribution of electric charges of different signs in space is due to the potential energy of their mutual attraction, which is a component in the Gibbs energy of a solution. Therefore, having calculated the energy of mutual attraction of ions, we can better understand all the thermodynamic properties of electrolytes and calculate a number of properties of dilute electrolytes.

It is natural that the electrostatic energy of mutual attraction of ions is also of great importance for the kinetic properties of ions (for example, for the electrical conductivity of electrolytes), which will be considered in Chap. 17.

In our brief exposition of the fundamentals of the statistical (electrostatic) theory of electrolytes, we shall first derive the equation for the electric potential of an ionic atmosphere, and then deal with the equations for the mean activity coefficients of electrolytes following from it.

The total potential $\varphi_t$ of the electric field around an ion consists of the potential $\varphi$ determined by the charge of this central ion and the potential $\varphi_a$ of the ionic atmosphere around it, namely.

$$\varphi_t = \varphi + \varphi_a$$

Our task is to find the values of $\varphi$ and $\varphi_t$ with the aid of equations of electrostatics and then determine the potential of the ionic atmosphere $\varphi_a$.

Let us consider the statistical distribution of ions in a solution with the relative permittivity $\varepsilon_r$ around an ion selected as the central one. Let it be a cation with the charge $q$. There is an electric field with spherical symmetry around this ion. The potential of the field at every point is a function of the distance $r$ to this point from the central ion.

According to Coulomb's law, the potential $\varphi_r$, i.e. the energy required to move a unit positive charge to point $r$ from infinity, is

$$\varphi_r = -\int_{\infty}^{r} \mathbf{E}\, dr = -\int_{\infty}^{r} \frac{q}{\varepsilon_r r}\, dr = \frac{q}{\varepsilon_r r} \tag{16.20}$$

where $\mathbf{E} = -\frac{d\varphi_r}{dr}$ is the field strength (intensity).

When a positive charge $q$ is moved from infinity to point $r$, its energy grows by $q\varphi_r = \frac{q^2}{\varepsilon_r r}$. For a negative charge $-q$ the change in the energy will be $-\frac{q^2}{\varepsilon_r r}$.

Let us find the total potential $\varphi_t$ at any point of space around the central ion. This potential is determined by the density of the charge at the given point and is created both by the central ion, which is considered to be stationary, and by the remaining ions, which move randomly. If the distribution of the electric charge in space changes continuously from point to point, the dependence of the field potential on the coordinates of the point is expressed by the Poisson equation[1]

$$\Delta\varphi_t \equiv \frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2} = -4\pi\frac{\rho}{\varepsilon_r} \tag{16.21}$$

where $\rho$ = density of charge continuously distributed in the field
$\Delta$ = Laplacian operator symbolizing differentiation of a function as shown in Eq. (16.21).

[1] The distribution of a charge in an electrolyte is not continuous if we consider small elements of the volume containing a small number of ions. Using the Poisson equation, we smooth out the microscopic discontinuity of the field in the electrolyte, which is permissible, since our final aim is to study macroscopic properties.

Let us now find the distribution of the charge density $\rho$ in the volume of the solution around a central ion, relating this quantity to the value of the total potential of the field $\varphi_t$ at each point of the solution.

The numbers of positive and negative ions in an element of volume $dV$ at a distance $r$ from the ion creating the field will be (in accordance with Boltzmann's distribution law)

$$N_A n_+ dV = N_A \bar{n}_+ e^{-q\varphi_t/kT} dV \quad \text{and} \quad N_A n_- dV = N_A \bar{n}_- e^{+q\varphi_t/kT} dV \quad (16.22)$$

where $\bar{n}_+$ and $\bar{n}_-$ = mean concentrations of the respective ions in the solution, i.e. the mean number of gramme-ions per cubic centimetre

$n_+$ and $n_-$ = actual concentrations of the respective ions, in the given element of volume

$N_A$ = Avogadro constant

$\varphi_t$ = field potential in element of volume $dV$

$k$ = Boltzmann constant.

The charge density, equal to the sum of the charges created by all the ions, is determined with the aid of Eq. (16.22):

$$\rho = \sum_i z_i q_e \bar{n}_i N_A e^{-z_i q_e \varphi_t/kT} \quad (16.23)$$

where $q_e$ = elementary charge (charge of an electron), which may be positive or negative

$z_i$ = charge number of ion $i$.

If only monovalent positive and negative ions are present, we have $\bar{n}_+ = \bar{n}_- = \bar{n}$, and

$$\rho = N_A \bar{n} q_e \left(e^{-q_e\varphi_t/kT} - e^{q_e\varphi_t/kT}\right) = 2N_A \bar{n} q \sinh \frac{q_e \varphi_t}{kT}$$

Using Eq. (16.23) for $\rho$ in the Poisson equation (16.21), we get

$$\Delta\varphi_t = -\frac{4\pi q_e}{\varepsilon_r} \sum_i z_i \bar{n}_i N_A e^{-z_i q_e \varphi_t/kT} \quad (16.24)$$

The field around an ion has spherical symmetry. For this reason we can replace the coordinates $x$, $y$ and $z$ in Eq. (16.21) by a single coordinate $r$, i.e. transfer to spherical coordinates. It should be remembered that the potential $\varphi_t$ depends only on the radius $r$ and does not depend on the angular coordinates. After transferring to spherical coordinates we get

$$\Delta\varphi_t = \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\varphi_t}{dr}\right) = -\frac{4\pi q_e}{\varepsilon_r} \sum_i z_i \bar{n}_i N_A e^{-z_i q_e \varphi_t/kT} \quad (16.24a)$$

Let us expand the exponential function in the right-hand parts of Eqs. (16.24) and (16.24a) into a series:

$$e^{-q_e z_i \varphi_t/kT} = 1 - \frac{q_e z_i \varphi_t}{kT} + \frac{q_e^2 z_i^2 \varphi_t^2}{2k^2T^2} \tag{16.25}$$

If $q_e z_i \varphi_t \ll kT$, the series rapidly converges and we can limit ourselves to its first two terms. This is obviously correct for sufficiently high temperatures and dilute solutions, where the value of $\varphi_t$ for ions arranged around the central ion is not great owing to the great values of $r$. Let us substitute Eq. (16.25) for the exponential function in Eq. (16.24a):

$$q_e \sum z_i \bar{n}_i N_A e^{-q_e z_i \varphi_t/kT} = N_A \sum z_i \bar{n}_i q_e \left(1 - \frac{q_e z_i \varphi_t}{kT}\right) \tag{16.25a}$$

In an electrically neutral solution $\sum z_i \bar{n}_i q_e = 0$[1] and the first term in the right-hand part of Eq. (16.25a) vanishes. Equation (16.24a) becomes

$$\Delta\varphi_t = \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\varphi_t}{dr}\right) = \frac{4\pi q_e^2 N_A}{\varepsilon_r kT} \sum_i z_i^2 \bar{n}_i \varphi_t \tag{16.26}$$

Let us introduce the symbol

$$\varkappa^2 = \frac{4\pi q_e^2 N_A}{\varepsilon_r kT} \sum z_i^2 \bar{n}_i \tag{16.27}$$

The quantity $\varkappa^2$ depends on the concentration of the solution and the temperature, but does not depend on the potential. Its physical meaning will be considered below. The quantity $\varkappa$ has the dimension of inverse length ($L^{-1}$). Introducing $\varkappa^2$, Eq. (16.26) becomes

$$\Delta\varphi_t = \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\varphi_t}{dr}\right) = \varkappa^2 \varphi_t \tag{16.28}$$

Integration of second-order differential equation (16.28) yields

$$\varphi_t = c_1 \frac{e^{-\varkappa r}}{r} + c_2 \frac{e^{\varkappa r}}{r} \tag{16.29}$$

From the condition that when $r = \infty$ the value of $\varphi_t$ becomes zero we get $c_2 = 0$. Now let us determine $c_1$, considering that the solutions are very dilute. In this case the distances between ions are very great in comparison with the radii of the ions, and the latter can be considered as points. A point ion with the charge $q_e z$, remote from other ions in an infinitely dilute solution, has the potential $\varphi = \frac{q_e z}{\varepsilon_r r}$ [see Eq. (16.20)]. For very small values of $r$

[1] Since terms with $z_i^2$ will be after the sum sign, the second term will not become equal to zero.

near a point ion the potential $\varphi_t$ from Eq. (16.29) should coincide with $\varphi$, i.e. when $r \to 0$

$$\varphi_t = c_1 \frac{e^{-\varkappa r}}{r} = \frac{q_e z}{\varepsilon_r r}$$

Hence $c_1 = \frac{q_e z}{\varepsilon_r}$, and

$$\varphi_t = \frac{q_e z}{\varepsilon_r} \frac{e^{-\varkappa r}}{r} \tag{16.30}$$

When $r > 0$ the quantity $\varphi_t$ is the sum of the potential $\varphi$ of an ion itself and the potential $\varphi_a$ of the ionic atmosphere. Hence

$$\varphi_a = \varphi_t - \varphi = \frac{q_e z}{\varepsilon_r} \frac{e^{-\varkappa r}}{r} - \frac{q_e z}{\varepsilon_r r} = -\frac{q_e z}{\varepsilon_r}\left(\frac{1-e^{-\varkappa r}}{r}\right) \tag{16.31}$$

Let us now express the charge density $\rho$ through $\Delta\varphi_t$ according to Eq. (16.21), using Eqs. (16.28) and (16.30):

$$\rho = -\frac{\varepsilon_r \Delta\varphi_t}{4\pi} = -\frac{\varepsilon_r \varkappa^2 \varphi_t}{4\pi} = -\frac{\varkappa^2 q_e z}{4\pi} \frac{e^{-\varkappa r}}{r} \tag{16.32}$$

Integrating $\rho$ over the entire volume (the distance $r$ from the central ion changes from 0 to $\infty$), we get the total charge of the field around one ion:

$$\int_0^\infty \rho 4\pi r^2\, dr = -\varkappa^2 q_e z \int_0^\infty r e^{-\varkappa r}\, dr = -q_e z$$

Thus the charge of the ionic atmosphere around one ion is equal to the charge of the central ion with the opposite sign. Let us write an expression for $1/\varkappa$ on the basis of Eq. (16.27), inserting into it instead of $n_i$ the concentration $c_i$ expressed in gramme-ions per $dm^3$ $\left(\bar{n}_i = \frac{c_i}{1000}\right)$:

$$\frac{1}{\varkappa} = \sqrt{\frac{\varepsilon_r kT}{8\pi q_e^2}} \frac{\sqrt{\frac{1000}{N_A}}}{\sqrt{\frac{1}{2}\sum_i z_i^2 c_i}} \tag{16.33}$$

The quantity $\frac{1}{2}\sum_i z_i^2 c_i$ will be called the *ionic strength* of the solution and designated by $I'$, which differs from the quantity $I$ in Eq. (16.19) [the difference between them will be dealt with below, see Eq. (16.46)]

$$I' \equiv \frac{1}{2}\sum_i c_i z_i^2 \tag{16.34}$$

The quantity $I'$ characterizes the total concentration of all the ions in a solution with account of the difference in the energies of

their interaction, proportional to the square of the charge number $z_i$. Thus

$$\frac{1}{\varkappa} = \sqrt{\frac{1000k}{8\pi q_e^2 N_A}} \sqrt{\frac{\varepsilon_r T}{I'}} \tag{16.35}$$

Constant quantities have been assembled under the sign of the first root. If we insert their values, we get

$$\frac{1}{\varkappa} = K \sqrt{\frac{\varepsilon_r T}{I'}} = 1.988 \times 10^{-10} \sqrt{\frac{\varepsilon_r T}{I'}} \tag{16.36}$$

A glance at Eq. (16.33) shows that the quantity $\varkappa$ is a function of the composition of a solution, its relative permittivity and temperature. This quantity characterizes the change in the density of the ionic atmosphere $\rho$ around the central ion with an increase in the distance $r$ from this ion. The quantity $1/\varkappa$ has the dimension of length. The smaller the value of $\varkappa$, the slower does the density of the charges $\rho$ in the ionic atmosphere change with an increase in $r$. The quantity $1/\varkappa$ can be defined (not quite accurately) as the effective radius of the ionic atmosphere[1].

Let us replace the ionic atmosphere around a central ion with a sphere having the charge $-zq_e$ and the potential $\varphi_a$ equivalent to the potential of the ionic atmosphere. The radius of such an imaginary sphere will obviously increase with a growth in the value of $1/\varkappa$.

The relative permittivity $\varepsilon_r$ of water at 18 °C is equal to 81.3. Assuming that $c = 0.01$, we get a value of $1/\varkappa$ ranging from $25 \times \times 10^{-8}$ to $100 \times 10^{-8}$ cm, depending on the charge numbers of the ions.

**16.6. Work of Formation of Ionic Atmosphere. Electrostatic Energy of Electrolyte.** Now we can find the potential energy of interaction of ions in a solution, which is determined by the mutual electrostatic attraction of the ions. This energy is an addend in the expression for the Gibbs energy of a solution.

Let us simplify Eq. (16.31) for the potential of an ionic atmosphere $\varphi_a$, expanding the exponential function into a series and limiting ourselves to one term of it:

$$\varphi_a = -\frac{q_e z}{\varepsilon_r} \varkappa \tag{16.37}$$

Let the charge of each ion $q_e z$ be formed by an increase in a variable charge $q$ from 0 to $q_e z$.

[1] The quantity $1/\varkappa$ formally corresponds to the distance along a straight line from the central ion over which the density of the ionic atmosphere drops approximately $e$ times.

Assuming that $q' = q_e \alpha z$, let us increase the charge $q'$ from 0 to $q_e z = q$ by continuously increasing the factor $\alpha$ from 0 to 1. The differential of the charge will be $dq' = q_e z\, d\alpha$.

It can be seen from Eq. (16.27) that when $q' = q_e \alpha z$ the quantity $\varkappa'$ is less than $\varkappa$ and is determined by the equation

$$\varkappa' = \sqrt{\frac{4\pi q_e^2 N_A}{\varepsilon_r kT}} \sqrt{\sum z_i^2 \alpha^2 n_i} = A\alpha \sqrt{\sum z_i^2 n_i} = \alpha\varkappa$$

Thus the value of $\varkappa'$ also grows with an increase in $\alpha$. Now, using Eq. (16.37), let us express the potential of an ionic atmosphere $\varphi_a'$ at a variable $q'$:

$$\varphi_a' = -\frac{q_e \alpha z}{\varepsilon_r} \varkappa' = -\frac{q_e \alpha^2 z}{\varepsilon_r} \varkappa \tag{16.38}$$

The change in the energy of interaction of an ionic atmosphere with a central ion of species $i$ as the charge of the latter changes, i.e. the work of formation of the ionic atmosphere[1], can be written as

$$dE_i = \varphi_a' dq' = -\frac{\alpha^2 q_e^2 z_i^2}{\varepsilon_r} \varkappa d\alpha \tag{16.39}$$

Integration of Eq. (16.39) gives the energy of formation of an ionic atmosphere:

$$E_i = -\int_0^1 \frac{q_e^2 z_i \varkappa \alpha^2\, d\alpha}{\varepsilon_r} = -\frac{q_e^2 z_i^2 \varkappa}{3\varepsilon_r} \tag{16.40}$$

The quantity $E_i$ relates to one ion and its ionic atmosphere. If we multiply Eq. (16.40) by $\bar{n}_i N_A$, where $\bar{n}_i$ is the number of gramme-ions in 1 cm$^3$, we get for all the ions in a solution

$$E_{el} = \sum \bar{n}_i N_A E_i = -\frac{q_e^2 N_A}{3\varepsilon_r} \sum_i \bar{n}_i z_i^2 \varkappa \tag{16.41}$$

Inserting into Eq. (16.41) the equation $\bar{n}_i = \frac{c_i}{1000}$ and expression (16.34), we get

$$E_{el} = -\frac{q_e^2 2 N_A}{3\varepsilon_r} \sum \frac{c_i z_i^2 \varkappa}{2 \times 1000} = -\frac{2}{3} \frac{q_e^2 N_A}{\varepsilon_r \times 1000} I' \varkappa \tag{16.42}$$

In Eqs. (16.41) and (16.42) the quantity $E_{el}$ is the electrostatic part of the Gibbs energy calculated for 1 cm$^3$ of a solution containing $\bar{n}_i N_A$ ions or $\bar{n}_i$ gramme-ions of each species $i$ (or $c_i$ gramme-ions per dm$^3$ of the solution).

[1] The electrostatic energy $E_{el}$ of a system is part of its free energy (the Helmholtz or Gibbs energy), since a change in $E_{el}$ is equal to the work $W$ of charging particles fixed in space or of the mutual directed motion of already charged particles at constant values of $p$ and $T$.

The energy of formation of an ionic atmosphere is a complicated function of the concentration of a solution, on which the quantities $I'$ and $\varkappa$ also depend. The energy of charging the central ion is also a part of the Gibbs energy of a solution, but it is directly proportional to the charge of the ion, and when calculating for a definite volume of a solution—directly proportional to the number of ions, i.e. the mass (the value of $\varphi$ itself does not depend on the concentration). Therefore, when we further find the chemical potential, i.e. in differentiation with respect to mass, this energy gives a constant addend included in $\mu_i^\circ$ that is independent of the concentration. We do not take this addend into consideration.

**16.7. Activity Coefficients of Electrolytes.** Infinitely dilute solutions are characterized by the fact that the heats of solution of salts in them are equal to zero, and the activity coefficients are constant and may be equated to unity [see Vol. 1, Sec. 6.8, Eq. (6.27)]. The addition of the solvent does not change the energy of an infinitely dilute solution of an electrolyte, since all the ions are at such a great distance from one another that their energy of interaction is practically constant (it does not depend on the dilution). On the other hand, all the ions in such a solution are completely solvated and the energy of interaction of the ions with the solvent molecules is also constant. In such an infinitely dilute solution for ions of species $i$ we have

$$\mu_{i,\,\mathrm{id}} = f(T) + RT \ln m_i = \mu_i^\infty + RT \ln m_i \qquad (16.43)$$

Consequently, in an infinitely dilute solution the quantity $\mu_i$ is linearly related to the logarithm of the molality $m_i$. Let us assume that the deviation from Eq. (16.43) for more concentrated solutions is due only to electrostatic interaction of the ions as they approach one another. This assumption is true only for dilute solutions (although more concentrated than infinitely dilute ones). The quantity $\gamma_i'$ for such solutions is not equal to unity, and Eq. (16.43) becomes

$$\mu_i = \mu_i^\infty + RT \ln a_i = \mu_i^\infty + RT \ln m_i + RT \ln \gamma_i' \qquad (16.44)$$

$$\mu_i = \mu_{i,\,\mathrm{id}} + RT \ln \gamma_i'$$

$$RT \ln \gamma_i' = \mu_i - \mu_{i,\,\mathrm{id}}$$

Here $\mu_{i,\mathrm{id}}$ corresponds to an imaginary infinitely dilute solution having the same molality $m_i$ as the real solution with an ionic activity coefficient $\gamma_i'$ being considered. The difference $\mu_i - \mu_{i,\mathrm{id}}$ is obviously equal to the fraction of the electrostatic energy $E_{\mathrm{el}}$ that falls to one mole of component $i$. In accordance with the definition of $\mu$ as the derivative of the Gibbs energy $G$ with respect to mass, to find $\mu_i - \mu_{i,\mathrm{id}}$ Eq. (16.42) for the electrostatic energy must be differentiated with respect to the number of moles of component $i$.

It is first necessary to find the relation between $\varkappa$ and $\bar{n}_i$. Let us differentiate Eq. (16.27) with respect to $\bar{n}_i$:

$$2\varkappa\frac{\partial\varkappa}{\partial\bar{n}_i}=\frac{4\pi q_e^2 N_A z_i^2}{\varepsilon_r kT}=\frac{\varkappa^2 z_i^2}{\sum\bar{n}_i z_i^2}$$

Hence

$$\frac{\partial\varkappa}{\partial\bar{n}_i}=\frac{z_i^2}{2\sum\limits_i\bar{n}_i z_i^2}\varkappa$$

Now let us differentiate Eq. (16.41) with respect to $\bar{n}_i$:

$$\left(\frac{\partial E_{el}}{\partial\bar{n}_i}\right)_V=-\frac{q_e^2 z_i^2 N_A}{3\varepsilon_r}\varkappa-\frac{q_e^2 z_i^2 N_A\varkappa}{6\varepsilon_r}=-\frac{q_e^2 z_i^2 N_A}{2\varepsilon_r}\varkappa \quad (16.45)$$

Using the expression for $\varkappa$ from Eq. (16.35) in Eq. (16.45), we get

$$\left(\frac{\partial E_{el}}{\partial\bar{n}_i}\right)_V=-\frac{q_e^2 z_i^2 N_A}{2\varepsilon_r}\sqrt{\frac{8\pi q_e^2 N_A}{1000k}}\sqrt{\frac{I'}{\varepsilon_r T}}=$$

$$=\frac{q_e^3 z_i^2 N_A}{\varepsilon_r^{3/2}T^{1/2}}\sqrt{\frac{2\pi N_A}{1000k}}\sqrt{I'} \quad (16.45a)$$

The left-hand part of Eq. (16.45a) is the derivative of the electrostatic energy of 1 cm³ of a solution with respect to the number of gramme-ions of species $i$, i.e. it is the electrostatic part of the chemical potential of component $i$.

For purposes of comparison with Eq. (16.44), where the measure of the concentration is the molality $m_i$, expression (16.34) for the ionic strength $I'$ must be transformed by inserting [see Vol. 1, Sec. 5.1, Eqs. (5.2) and (5.2a)]

$$c_i=\frac{m_i 1000\rho}{1000+m_i M_i}$$

where $\rho$ is the density of a solution, g/cm³.

For sufficiently dilute solutions when $m_i M_i \ll 1000$ we have

$$c_i = m_i\rho_0$$

where $\rho_0$ is the density of the pure solvent. Inserting the last expression into Eq. (16.34), we get

$$I'=\frac{1}{2}\sum m_i z_i^2\rho_0=I\rho_0 \quad (16.46)$$

The symbol $I$ denotes the ionic strength expressed through the molality $m_i$, i.e. $I=\frac{1}{2}\sum m_i z_i^2$. We see that in dilute aqueous solutions, where $\rho\approx\rho_0\approx 1$ we have $I'=I$. It should be remembered

that for non-aqueous solutions the quantities $I'$ and $I$ are not equal to each other.

To compare Eq. (16.45a), in which we assume that $I' = I$, with Eq. (16.44), let us divide the former by $RT$. Hence

$$\frac{1}{RT}\left(\frac{\partial E_{el}}{\partial \bar{n}_i}\right)_V = \ln \gamma_i' = -\frac{q_e^3 z_i^2}{\varepsilon_r^{3/2} T^{3/2} k^{3/2}} \sqrt{\frac{2\pi N_A}{1000}} \sqrt{I'}$$

whence

$$\log \gamma_i' = -\frac{1.823 \times 10^6 z_i^2}{(\varepsilon_r T)^{3/2}} \sqrt{I'} \tag{16.47}$$

For the substance $M_{\nu_+}N_{\nu_-}$ that dissociates according to the equation

$$M_{\nu_+}N_{\nu_-} = \nu_+ M^{z+} + \nu_- N^{z-}$$

in accordance with the definition of the mean ionic activity coefficient (16.17a), we have

$$\log \gamma_\pm' = \frac{\nu_+ \log \gamma_+' + \nu_- \log \gamma_-'}{\nu_+ + \nu_-} \tag{16.47a}$$

Inserting this expression into Eq. (16.47), we get[1]

$$\log \gamma_\pm' = -\frac{1.823 \times 10^6}{(\varepsilon_r T)^{3/2}} \left(\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-}\right) \sqrt{I'} =$$

$$= -\frac{1.823 \times 10^6}{(\varepsilon_r T)^{3/2}} z_+ z_- \sqrt{I'} = -A z_1 z_2 \sqrt{I'} \tag{16.48}$$

If $T = 298$ °C, then $\varepsilon_r$ for pure water is equal to 78.25 and, consequently, $A = 0.5117$.

According to the electrostatic theory of electrolytes, the dependence of $\log \gamma_\pm'$ on the square root of the ionic strength is a linear one. This was confirmed by numerous experimental investigations of electrolytes with very low concentrations. It follows from everything said above that Eq. (16.48) is true only for greatly diluted solutions, since in deducing the equation for the potential of an ionic atmosphere certain essential mathematical simplifications and physical assumptions were made. Equation (16.48) is called the *Debye-Hückel limiting law* or the *first approximation of the Debye-Hückel theory* for $\gamma_\pm'$. The coefficient $A$ depends on the temperature (directly or in terms of the relative permittivity $\varepsilon_r$). Checking of the Debye-Hückel limiting law at low concentrations (low values

[1] The expression in brackets is transformed as follows. For an electrically neutral molecule $\nu_+ z_+ = \nu_- z_-$. In the numerator of the fraction we replace $\nu_+ z_+$ by $\nu_- z_-$ and vice versa:

$$\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-} = \frac{\nu_- z_- z_+ + \nu_+ z_+ z_-}{\nu_+ + \nu_-} = \frac{(\nu_- + \nu_+) z_+ z_-}{\nu_+ + \nu_-} = z_+ z_-$$

of $I'$) showed that it well describes the relation of the slope of the straight line $\log \gamma'_{\pm} = f\,(I')^{1/2}$ to the product $z_1 z_2$ for salts of various valence types, and also the relation of the slope of the line to the relative permittivity of various solvents (if $\varepsilon_r$ is not too low).

For great concentrations the limiting law shown by Eq. (16.48) must be written in a more complicated way. By assuming that ions are point charges, we arrive at serious errors already at $m = 0.1$, when $1/\varkappa$ is appoximately equal to $2 \times 10^{-8}$ cm, i.e. the radius of an ionic atmosphere is commensurable with the dimensions of the ions. Since it is impossible for ions to infinitely approach one another, Debye and Hückel introduced a correction into the expression for the potential of an ionic atmosphere [see Eq. (16.37)]:

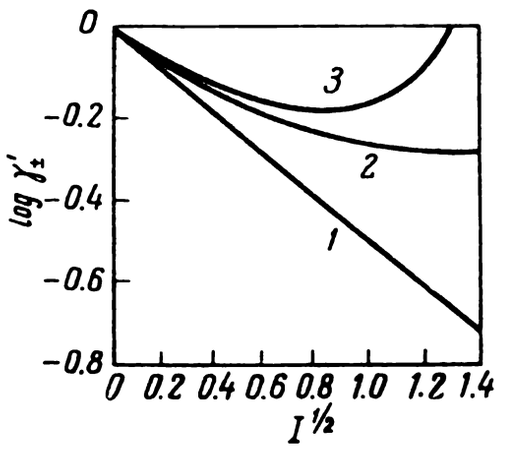


Fig. 16.4. Dependence of $\log \gamma'_{\pm}$ on $I^{1/2}$ calculated according to different equations of the Debye-Hückel law:
1 — Eq. (16.48); 2 — Eq. (16.50); 3 — Eq. (16.52)

$$\varphi_a = -\frac{q_e z_m}{\varepsilon_r}\,\varkappa\,\frac{1}{1+a\varkappa} \qquad (16.49)$$

where $a$ has the dimension of length and can be conventionally called the *mean effective diameter of the ions*. It is difficult to exactly define the physical meaning of this quantity because of a number of assumptions. For this reason $a$ is actually an empirical constant of the theory.

To deduce a more accurate equation for the electrostatic energy of ions we shall use Eq. (16.49) instead of Eq. (16.37). Next we shall find a more accurate expression for $\log \gamma'_{\pm}$. This will give us the following expression instead of Eq. (16.48):

$$\log \gamma'_{\pm} = -\frac{A z_1 z_2 \sqrt{I'}}{1 + Ba\sqrt{I'}} \qquad (16.50)$$

The coefficient $B$ changes slightly with the temperature. For aqueous solutions it equals $(0.32\text{-}0.33) \times 10^8$. Since the mean diameter of an ion is equal to $(3\text{-}4) \times 10^{-8}$ cm, the product $Ba$ for aqueous solutions is close to unity. For low values of $I'$ the product $Ba$ in the denominator of Eq. (16.50) can be taken equal to unity. For aqueous solutions $I' = I$, therefore

$$\log \gamma'_{\pm} = -\frac{A z_1 z_2 \sqrt{I}}{1 + \sqrt{I}} \qquad (16.51)$$

The empirically selected values of $a$ in Eq. (16.49) are usually of the same order as the diamater of the ions in a crystal lattice, but

frequently they are greater, sometimes smaller or even negative. To take account of the polarization of dipole molecules of the solvent around the solute ions (which is equivalent to reducing the relative permittivity $\varepsilon_r$ near an ion), another correction (the term $CI$) is introduced into the Debye-Hückel limiting law [Eq. (16.48)]. The result is the Hückel equation

$$\log \gamma'_{\pm} = -\frac{Az_1z_2\sqrt{I}}{1+Ba\sqrt{I}} + CI \qquad (16.52)$$

The constant $C$ is selected empirically.

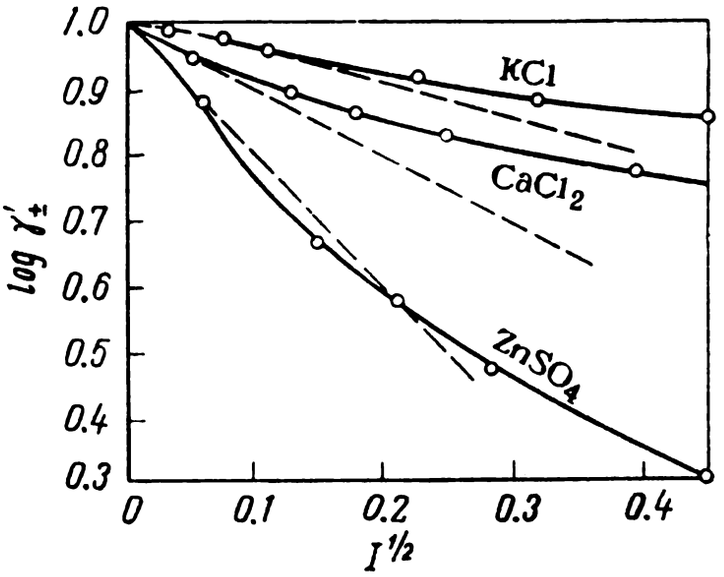


Fig. 16.5. Equation of the Debye-Hückel limiting law and experimental values of $\gamma'_{\pm}$

Figure 16.4 shows $\log \gamma'_{\pm}$ versus $I^{1/2}$ for various values of $A$, $Ba$ and $C$. Curve *1* corresponds to Eq. (16.48) of the Debye-Hückel limiting law, curve *2* to Eq. (16.50) and curve *3* to Eq. (16.52). The linear nature of the dependence of $\log \gamma'_{\pm}$ on $I^{1/2}$ at low concentrations can be seen in Fig. 16.5. The slopes of the straight lines (at $I \to 0$) are different for salts of different valence types (1-1, 1-2, 2-2).

Equation (16.52) was obtained by introducing corrections into Eq. (16.48) of the Debye-Hückel limiting law. It would be more consistent to precise the deduction of Eq. (16.26) by using several terms of the expansion of the exponential function for the potential [see Eqs. (16.24) and (16.25)]. The equations obtained are very complicated, however, and the results of calculations do not satisfy the requirements of thermodynamics. For this reason wide use is made of Eq. (16.52) and similar ones.

The development of the statistical theory of electrolytes was a step forward in comparison with Arrhenius's original theory of electrolytic dissociation. It takes into account the electrostatic interaction of ions and makes it possible to quantitatively characterize the dependence of the activity coefficients for ionic substances in a solution and the electrical conductivity of these solutions on the concentration at great dilution.

The complicated nature of accurate mathematical solutions makes it difficult to apply the electrostatic theory to more concentrated solutions, but it is developing in this direction. The main drawback of the electrostatic theory is the fact that practically no account is taken of the interaction of the ions with the molecules of the solvent. The use of the relative permittivity as a macroscopic characteristic of a solution does not make it possible to take into account the electrical interaction of the ions with the dipole molecules of the solvent at small distances. This drawback also limits the applicability of the Debye-Hückel theory to dilute solutions, in which the interaction of each ion with molecules of the solvent is complete and remains practically unchanged upon a further reduction of the concentration (dilution).

Recently the theory of solutions has received an improved mathematical foundation in the form of N. Bogolyubov's method, on the basis of which the theory of electrolytes has begun to develop further with considerable success.

**16.8*. Ionic Pairs and Triplets.** The equations of the electrostatic theory for the activity coefficient, and also for the electrical conductivity, were derived on the assumption that strong electrolytes are completely dissociated. Using the basic postulates of the electrostatic theory, we can introduce the conception of *ionic pairs*, which in some respects are similar to undissociated molecules. This conception was first developed by V. Semenchenko (1922) and independently by J. Brönsted (1926).

An ionic pair is formed when a cation and an anion approach each other until the distance between them is less than the known critical distance $l_{cr}$ determined by the equation

$$l_{cr} = \frac{z_1 z_2 e^2}{2\varepsilon_r kT}$$

The potential energy of two oppositely charged ions at this distance is equal to $2kT$. The kinetic energy is not sufficient to overcome the mutual attraction. The ions remain bound in a pair that does not participate in the conduction of electricity, although it is not a true molecule. It is possible to calculate the number of ions around a central ion of the opposite sign between the critical distance $l_{cr}$ and the distance of closest approach (collision diameter). In this way we determine the number of ionic pairs, the degree of their dissociation and the dissociation constant of the ionic pairs according to the mass action law. The critical distance in water at 25 °C for a mono-monovalent electrolyte is not great ($l_{cr} = 3.57$ Å), the number of ionic pairs is very small, and there is almost complete dissociation. For ions with great charges, and also in a solvent with a low relative permittivity, $l_{cr}$ has greater values, and association grows. Association also depends on the radii of the ions and increases with a decrease of these radii (i.e. with a growth in the distance of closest approach). Thus, in solutions of $LaFe(CN)_6$ in mixed solvents whose relative permittivity $\varepsilon_r \leqslant 57$, the dissociation constant of the ionic pairs decreases with a reduction in $\varepsilon_r$ in quantitative agreement with theory. This decrease in the constant ranges from $10^{-3}$ to $10^{-5}$. In a solution with $m = 0.01$, the degree of dissociation of the ionic pairs changes from 0.3 to 0.03 with a reduction in $\varepsilon_r$. The number of ionic pairs is very great. In aqueous solutions with $\varepsilon_r = 81$ the content of ionic pairs at low concentrations is a fraction of a per cent.

Developing the conception of ionic pairs, we can consider the formation of triplets and quadruplets. Triplets are formed when an ionic pair approaches a third ion

$$B^-A^+ + B^- = [B^-A^+B^-]^-$$
$$A^+B^- + A^+ = [A^+B^-A^+]^+$$

The possibility of the formation of an ionic triplet is determined not only by the energy conditions, but also by the mutual arrangement of the approaching ions.

Quadruplets are formed from ionic pairs:

$$2\,[A^+B^-] = \begin{bmatrix} A^+B^- \\ B^-A^+ \end{bmatrix}$$

The conception of triplets and the theory of triplet equilibria are used to explain the anomalous curves of electrical conductivity. For solutions with a low relative permittivity (water-dioxane mixtures), data on their electrical conductivity make it possible to establish the presence of ionic pairs and triplets, their concentrations and dissociation constants. Such formations as $BaCl^+$, $AgCl_2^-$ and $LiCl_2^-$ were found even in aqueous solutions.

The difference between ions and complex ions on one hand and ionic pairs and triplets on the other is apparently a quite subtle one and is sometimes difficult to establish. Complex ions should give special lines in spectra of combined dispersion, while these lines should be absent for typical ionic pairs.

**16.9*. Interaction of Ions with Solvent Molecules.** To date the complicated molecular interactions in electrolytes are still far from being explained. The molecular structure of electrolytes is interpreted differently. To give an idea of the present state of this problem, let us consider some different viewpoints.

When substances having ionic crystal lattices are dissolved in liquids with a high relative permittivity, the ions forming the surface layer of the lattice and the dipole molecules of the solvent mutually attract one another. The force of attraction $F$ can be expressed by the equation

$$F = -\frac{\mu_1 e_2}{r^3} \tag{16.53}$$

where $\mu_1$ = dipole moment of a solvent molecule
$e_2$ = charge of an ion
$r$ = distance between an ion and the end of a dipole closest to it.

Equation (16.53) is easily derived on the basis of Coulomb's law but it holds only for distances $r$ that are sufficiently great in comparison with the length of a dipole.

In the process of solution, the ions approach neighbouring solvent molecules as a result of attraction. Their potential energy decreases and heat is liberated. Solution is accompanied by compression, which can be considered as compacting of the solvent around the ions and the formation near each ion of a layer of solvent molecules that are bound closer to the ion. This process is called *solvation*.

It is expedient to call the action of an ion on the closest molecules of the solvent, which lose their independent translational motion and move together with the ion as a single kinetic unit, *primary solvation*.[1] A complex of these molecules form a *solvation shell*. *Secondary solvation* denotes the action of an ion on more remote solvent molecules that affects the structure of the solvent as a whole and the macroscopic properties of the solution.

Solvation of a proton has a specific nature. The first step of the interaction of a proton with a solvent should be considered as a chemical reaction. The ions formed are called lyonium ions:

$$\left.\begin{array}{l} H^+ + H_2O = H_3O^+ \text{ — hydroxonium ion} \\ H^+ + C_2H_5OH = C_2H_5OH_2^+ \text{ — ethoxonium ion} \end{array}\right\} \text{lyonium ions}$$

The lyonium ions thus formed solvate further similar to other ions.

Let us consider some phenomena accompanying the solution of ions. The total change in a property of a solution in comparison with the properties of the complex of the pure components (for example, water and salt) when reduced to a constant mass of the solution or solvent naturally grows with an increase in the ion concentration. But when calculating the total changes in the property per unit of mass of the solute (for example, per mole), the properties of very dilute solutions change particularly sharply. This is easy to understand, since in these conditions the distances between the ions are sufficiently great, and the other ions do not influence the action of the given ion on the solvent, which manifests itself completely. With an increase in the concentration, the action of separate ions on a given portion of the solvent begins to overlap and is partly neutralized. The "competition of the ions for the solvent" grows and the effect per mole of solute decreases.

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[1] The molecules of the solvation shell retain vibrational motion mainly in a radial direction, circular motion in the shell and limited rotational motion.

*Volume Effect of Solution.* The apparent volume $\psi_2$ of one mole of the solute in the solution is calculated on the assumption that the solvent is not compressed upon solution of the salt, i.e. that

$$V = n_1 v_1^\circ + n_2 \psi_2 \tag{16.54}$$

where $n_1$ and $n_2$ = numbers of moles of solvent and solute, respectively
$V$ = volume of solution
$v_1^\circ$ = volume of one mole of pure solvent.

It is actually the ions that are practically incompressible. By comparing the volume of one mole of a salt in a crystal with the apparent volume of the ions of one mole of this salt in a solution, we can determine the compression of the solvent reduced to one mole of the dissolved salt. Table 16.3 gives the values of the molar volumes of selected salts $v_2^\circ$ in the crystalline state and the apparent molar volumes $\psi_2^\infty$ of the salts in aqueous solutions for infinite dilution. The difference between these quantities $\psi_2^\infty - v_2^\circ$ is equal to the change in the volume of the solution when one mole of the salt is dissolved in an infinitely great amount of water.

TABLE 16.3

**Apparent Volumes of Dissolved Salts and Molar Expansions in Dissolving**

| Salt | Volumes, cm³/mol | | |
|---|---|---|---|
| | $v_2^\circ$ | $\psi_2^\infty$ | $\psi_2^\infty - v_2^\circ$ |
| $CuSO_4$ | 44.27 | —4.9 | —49.2 |
| $MgSO_4$ | 45.12 | —1.7 | —46.8 |
| $K_2CO_3$ | 56.93 | 8.55 | —48.38 |
| NaOH | 18.78 | —3.75 | —22.53 |
| $K_2Cr_2O_7$ | 109.3 | 92.45 | —16.85 |
| $NH_4C_2H_3O_2$ | 71.83 | 60.72 | —11.11 |
| NaCl | 27.02 | 16.28 | —10.74 |
| LiCl | 20.50 | 17.02 | —3.48 |

The quantities $\psi_2^\infty - v_2^\circ$ are negative and indicate compression of an electrolyte solution when it is being formed. The compression is sometimes so great that the quantity $\psi_2^\infty$ itself is negative. This means that the compression is greater than the volume of the solid salt, and the volume of the water taken for the solution is greater than that of the solution obtained.

It is easy to understand the compression of electrolytes as a manifestation of *electrostriction*. This is the name given to the compression of dielectrics in an electric field. This phenomenon is the opposite of the piezoelectric effect. Obviously, the compression of the solvent is especially great near the surface of an ion, where the electric field reaches an enormous value. The compression diminishes in the parts of the solvent farther from an ion. Using the theory of electrostriction, we can compute the distribution of the effective additional pressure around an ion. The electrostatic forces can be so replaced by this pressure as to result in the same compression of the solvent. This pressure at distances from the centre of an ion ranging between 0.8 and 12 Å changes from $5 \times 10^3$ to 0.5 bar (1 bar = $= 10^5$ N/m² $\approx$ 1 atm). The calculation of the compression under these pressures

with account taken of polarization gives values of the same order as experimental ones.

*Heat Capacity of Electrolytes.* The heat capacities of electrolyte solutions, as well as their volume, are less than the additive value, i.e. the heat capacity of the solvent in dissolving of a solute decreases. This decrease corresponds to that which would occur in the absence of the solvating action of the ions on the solvent, but in the presence of a pressure gradient around the ions as indicated above. It is general knowledge that a growth in the pressure at room temperatures results in an appreciable reduction of the heat capacity of water.

*Energy (Heat) of Solvation.* The energy of solvation of ions can be calculated by comparing the molar values of the energy of an ionic lattice $U$[1] and the heats of solution of a salt $Q_{sol}$. The difference between these quantities is equal to the heat of solution of free (gaseous) ions of one mole of a substance (the heat of solvation $Q_{solv}$):

$$Q_{solv} = -U + Q_{sol} \tag{16.55}$$

The heat of solution may be positive or negative depending on the type of salt. The heat of solvation is always negative, i.e. in solvation heat is liberated.

Table 16.4 gives the heats of solvation of selected salts in water and alcohols.

TABLE 16.4

**Heats of Solvation $Q_{solv}$ of Selected Salts in Water and Alcohols (according to K. Mishchenko)**

| Salt | $Q_{solv}$, kcal/mol | | |
|---|---|---|---|
| | in water | in methanol | in ethanol |
| LiCl | −213 | −216 | −217 |
| NaCl | −186 | −189 | — |
| NaBr | −175 | −179 | −178 |
| NaI | −134 | −170 | −169 |
| KI | −144 | — | −148 |

Thermodynamic calculations of the entropy of a solvent in a solution show that the entropy of water decreases when ions are dissolved in it (at low concentrations). This circumstance also corresponds to the notion that the ions bind the water molecules into a primary solvation shell (an increase in the ordered nature of distribution of the molecules results in diminishing of the entropy)[2].

In strong electrolytes with great dilution many quantities characterizing the properties of solutes are found to be additive ones, i.e. summated from the corresponding properties of the ions. Among these quantities are the apparent volume of a salt, the heat of hydration, and the compressibility. This is natural, since upon the complete dissociation of a salt in a dilute solution the properties of some ions do not affect in any way the interaction of other ions with the solvent. However, representation of a measured (more exactly, of a computed from

[1] By the energy of an ionic lattice $U$ is meant the decrease in energy in the isothermal formation of a lattice from ideal ion gases. This quantity is of the order of hundreds of kilocalories per mole (see Vol. 1, Sec. 2.3).

[2] At great concentrations of the ions the entropy of the solvent grows. This will be taken into account later.

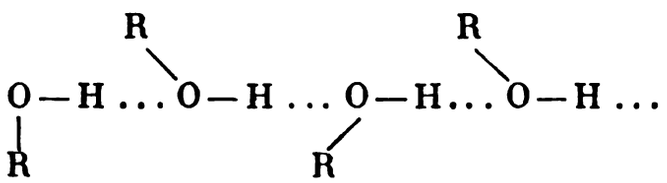
the results of measurements) thermodynamic property of a dissolved salt as the sum of the properties of the ions of this salt and finding of the value of the addends of this sum are impossible without using a more or less arbitrary assumption. The heats (energies) of hydration of separate ions can be obtained from the heats of hydration of the salts calculated according to Eq. (15.55) if we assume that the energies of hydration of the $K^+$ and $Cl^-$ ions are equal (with account of the difference in the orientation of the water molecules near the anion and the cation). Another method of determining the heats of hydration consists in so selecting the additive terms that the values of the solvation energies of the ions linearly depend on quantities that are reciprocals of the ion radii. The heats of hydration of an ion computed in different ways semiquantitatively agree with one another. The heats of hydration of monovalent ions have values of the order of 70-120 kcal/g-ion, of bivalent ones—300-500 kcal/g-ion, and of trivalent ones—600-1200 kcal/g-ion. The heat of complete hydration of a proton is equal to 260 kcal/g-ion.

*Molecular Structure of Aqueous Solutions.* Let us now acquaint ourselves with certain main results of the experimental investigation of the molecular structure of polar solvents and ionic solutions. The main experimental methods are x-ray structural analysis, investigation of absorption spectra and other optical methods.

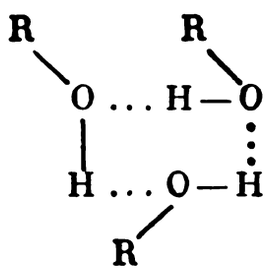
According to J. Bernal and R. Fowler, every molecule of water is bound to four other molecules (a tetrahedral configuration) by a hydrogen bond.

There is a vacant space between molecules in the form of a channel of a considerable diameter. Not only ring structures similar to that considered above are possible, but also chains of dipole molecules.

Alcohols obviously contain both chains of molecules of the type



and closed complexes



Molecules of the first type have a considerable summary dipole moment (polar association). For the second, the moment is much smaller (non-polar association).

Ions introduced into a polar liquid violate the structure of the solvent at great distances around the ions. This is indicated by the results of x-ray and spectroscopic investigations of solutions and by certain other facts (for example, the increase in the entropy of the solvent at high concentrations of the ions). The destructive action of large ions on the structure of water is especially noticeable, while small ions occupy the voids in the molecules of the water and change its structure very little. The coordination number of ions of a medium size, especially monovalent ones, is equal to four in dilute solutions. They obviously simply displace molecules of water as a whole without changing the structure of the latter. True, they attract and orient the nearest molecules of water and, forming a solvation shell, somewhat distort the structure of the water in the closest proximity (the volume, heat capacity, entropy and compressibility of the solution decrease). We can consider, however, that the structure of water in a solution is distorted insignificantly and even in a solvation shell is like the structure of pure water.

Thus the influence of ions on the structure of water can be considered as the sum of two different actions: firstly, the formation of solvation shells, which is accompanied by compression and a reduction of the entropy, and, secondly, the destruction of the molecular structure of water by the ions, especially large ones and at high concentrations,which leads to an increase in the entropy.

It is quite possible that a solvation shell is not a dense layer of oriented molecules, as is frequently imagined. In this connection the motion of the ions in a solution can also be imagined in a different way than the one described above. It is possibly a series of activated translational jumps of an ion from one position of equilibrium between the water molecules to a neighbouring one that is free at the given moment.

An ion must overcome an energy barrier for such a jump, i.e. have an additional activation energy that is the greater, the higher is the energy of interaction of an ion with molecules of water. The greater this barrier, the smaller the fraction of ions that at each given moment have the energy necessary for transition to the neighbouring equilibrium position and, obviously, the smaller is the mean mobility of the ions in an electric field. The latter only guides in a definite direction the activated translational jumps that in the absence of a field are performed chaotically in all directions. The above considerations do not agree with the simplified notion of an ion moving together with a solvation shell in a homogeneous viscous medium with a constant (in an electric field) velocity.

# CHAPTER 17

## ELECTRICAL CONDUCTANCE OF ELECTROLYTES

**17.1. Conductivity of Electrolytes.** The electrical conductance $G$ is a quantity that is the reciprocal of the electrical resistance $R$. Since

$$R = \rho \frac{l}{A}$$

then

$$G = \frac{1}{\rho} \frac{A}{l} = \varkappa \frac{A}{l} \tag{17.1}$$

where $\rho$ = resistivity
$l$ = distance between electrodes
$A$ = area of an electrode
$\varkappa$ = conductivity.

The conductivity $\varkappa$ of a liquid is the electrical conductance of one cubic centimetre of solution between flat electrodes having the same very great area (expressed in $cm^2$) and spaced 1 cm apart. The cubic centimetre of solution should be far from the edges of the electrode.

The conductivity is obviously the reciprocal of the resistivity.

TABLE 17.1

**Conductivity $\varkappa$ of Selected Substances at 18 °C**

| Substance | $\varkappa$, $\Omega^{-1}$ cm$^{-1}$ | Substance | $\varkappa$, $\Omega^{-1}$ cm$^{-1}$ |
|---|---|---|---|
| *Electronic Conductors* | | *Electrolytic Conductors* | |
| Silver | 615 000 | KCl, aq, 1 N | $9.789 \times 10^{-2}$ |
| Aluminium | 360 000 | KCl, aq, 0.1 N | $1.1167 \times 10^{-2}$ |
| Platinum | 86 200 | KCl, aq, 0.01 N | $1.2205 \times 10^{-3}$ |
| Mercury | 10 460 | Ethyl alcohol | $3.0 \times 10^{-6}$ |
| Retort carbon | 200 | Water | $4.3 \times 10^{-8}$ |
| *Electrolytic Conductors* | | *Dielectrics* | |
| NaCl(lq) at 750 °C | 3.40 | Sulphur | $2 \times 10^{-16}$ |
| $\alpha$-AgI(s) at 150 °C | 1.33 | Quartz | $5 \times 10^{-17}$ |
| $AgNO_3$(lq) at 209 °C | 0.65 | Paraffin | $10^{-18}$ |
| $H_2SO_4$, aq, 30% | 0.740 | | |

Table 17.1 gives experimentally found values of the conductivity of selected substances.

A glance at the table shows that on one hand electrolytes have a conductivity that is tens and hundreds of times smaller than that of metals, and on the other hand their conductivity, even for such poor electrolytic conductors as water or ethyl alcohol, is many orders greater than that of typical dielectrics.

A curve showing the dependence of the conductivity of solutions on the concentration usually has a maximum. Figure 17.1 shows curves of conductivity versus concentration for selected strong electrolytes, and also for a weak electrolyte—a solution of $CH_3COOH$. The presence of maxima on the curves becomes clear if we take into account that the velocity of the ions in dilute solutions of strong electrolytes is practically independent of the concentration, and the conductivity grows almost directly proportional to the number of ions. The latter, in turn, grows with the concentration. In concentrated solutions of strong electrolytes the ionic atmosphere appreciably reduces the velocity of the ions, and the conductivity decreases. In weak electrolytes the density of the ionic atmosphere is low and the velocity of the ions depends only slightly on the concentration. An increase in the concentration of the solution, however, is accompanied by an appreciable reduction in the degree of dissociation. This leads to a decrease in the concentration of the ions and to diminishing of the conductivity.

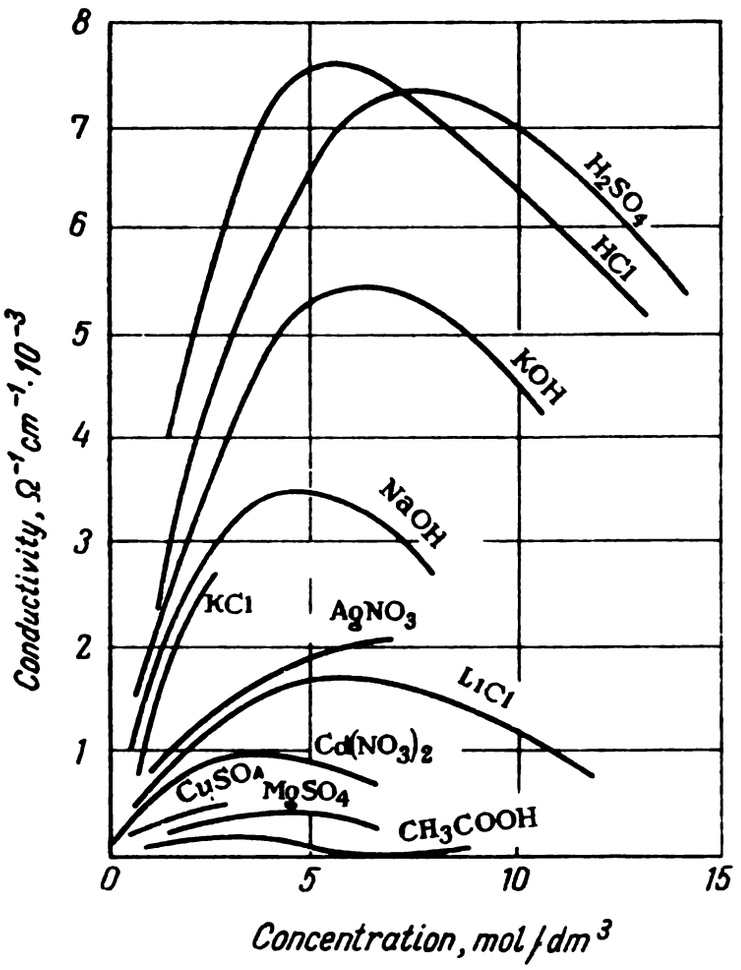



Fig. 17.1. Conductivity versus concentration for solutions of selected electrolytes

Curves similar to the ones shown in Fig. 17.1 are used in industrial conditions to select an electrolyte with the highest conductivity whose use makes it possible to reduce the consumption of electrical energy.

**17.2. Equivalent Conductivity.** The *equivalent conductivity* $\Lambda$ is found from the relation

$$\Lambda = \frac{1000\varkappa}{c} \text{ cm}^2/\text{g-eq}\cdot\Omega \qquad (17.2)$$

where $c$ is the equivalent concentration of the electrolyte, g-eq/dm$^3$.

*The equivalent conductivity is the conductance of such a volume* ($\varphi$ *cm*$^3$) *of a solution that contains 1 g-eq of the solute, the electrodes being 1 cm apart.* In view of what has been said above relative to the conductivity, we can imagine parallel electrodes 1 cm apart having a very great area and immersed into a solution. Let us imagine an area equal to $\varphi$ cm$^2$ cut on the surface of each electrode far from its edges. The conductance of the solution confined between the cut-out surfaces of such electrodes having an area of $\varphi$ cm$^2$ is the equivalent conductivity of the solution. The volume of the solution between these electrode areas is obviously equal to $\varphi$ cm$^3$. It contains one gramme-equivalent of salt. The quantity $\varphi$ equal to $1000/c$ cm$^3$/g-eq is called the *dilution*. There is always 1 g-eq of the solute between electrodes designed as indicated above at any concentration of the electrolyte, and the change in the equivalent conductivity due to the change in the concentration is connected only with a change in the number of ions formed by one gramme-equivalent, i.e. with a change in the degree of dissociation and a change in the velocity of the ions caused by the ionic atmosphere.

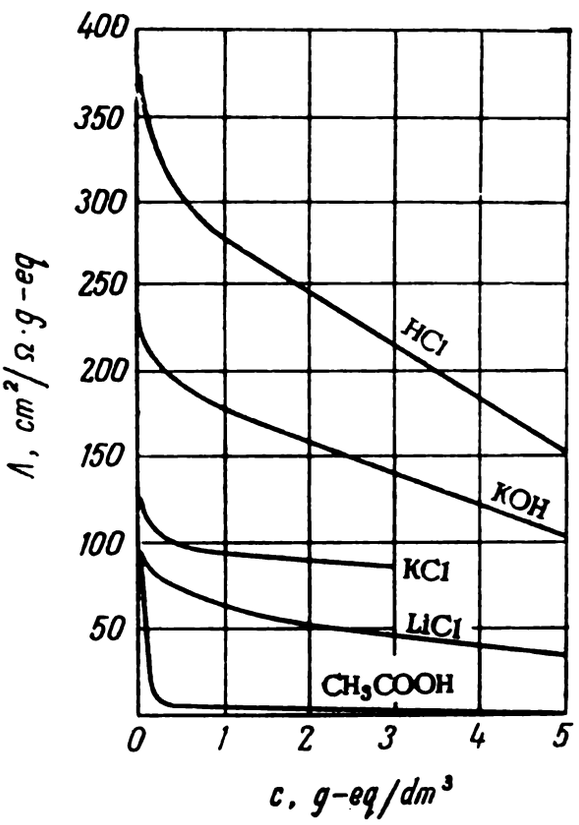



**Fig. 17.2. Equivalent conductivity versus concentration for solutions of selected electrolytes**

*The molar conductivity of an electrolyte* is the product of the equivalent conductivity and the number of gramme-equivalents per mole of dissociating substance.

Figure 17.2 shows the dependence of the equivalent conductivity on the concentration for selected electrolytes. It can be seen from the figure that with a growth in $c$ the value of $\Lambda$ first drops sharply, and then more smoothly. Of interest are plots of $\Lambda$ versus $\sqrt{c}$ (Fig. 17.3) and $\Lambda$ versus $\varphi$ (Fig. 17.4). A glance at Fig. 17.3 shows that for strong electrolytes $\Lambda$ slowly falls off linearly with a growth in $\sqrt{c}$,

which corresponds to Kohlrausch's empirical formula (1900):

$$\Lambda = \Lambda_\infty - A\sqrt{c} \tag{17.3}$$

where $\Lambda_\infty$ = limit equivalent conductivity at infinite dilution, i.e. $c \to 0$ and $\varphi \to \infty$

$A$ = constant.

It can be seen from Fig. 17.4 that the value of $\Lambda$ for strong electrolytes grows with an increase in $\varphi$ and asymptotically approaches $\Lambda_\infty$ [see Eq. (17.3)]. For weak electrolytes ($CH_3COOH$) the value of $\Lambda$ also grows with an increase in $\varphi$, but the approach to a limit and the value of the limit cannot practically be established in the majority of cases. Everything said above relates to the conductivity of aqueous solutions. These laws remain in force for electrolytes with other solvents, but there are also deviations from them. For example, a minimum is often observed on curves of $\Lambda$ versus $c$ (anomalous conductivity).

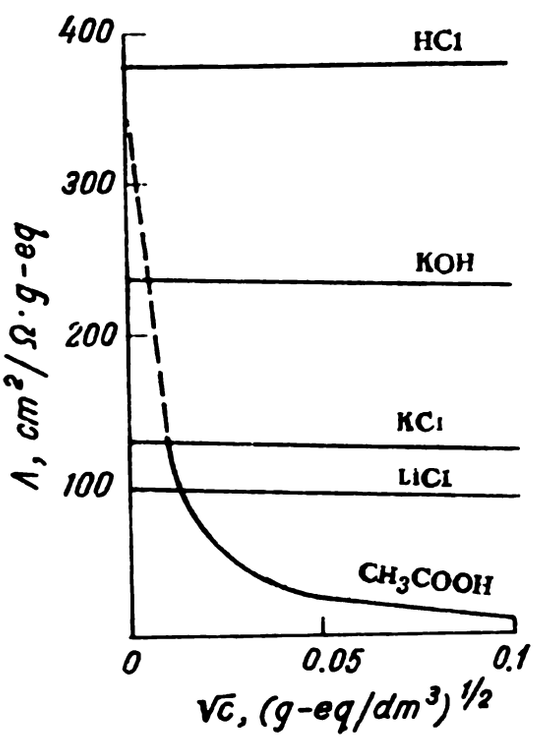



Fig. 17.3. Dependence of $\Lambda$ on $\sqrt{c}$ for solutions of selected electrolytes

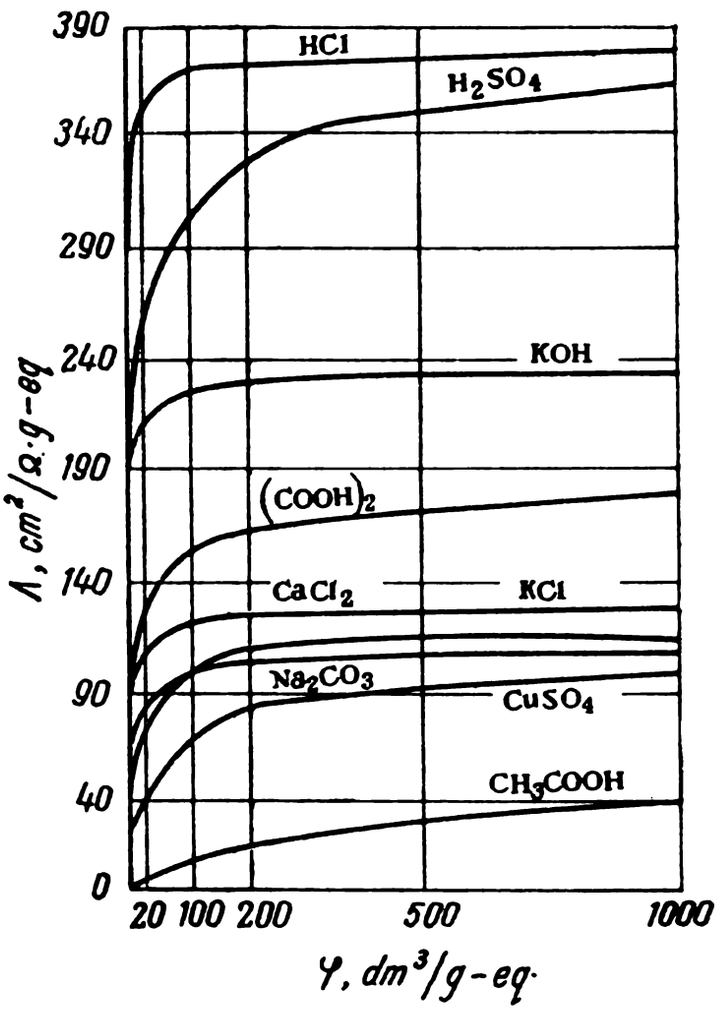



Fig. 17.4. Equivalent conductivity versus dilution for solutions of selected electrolytes

**17.3. Mobility of Ions.** Let us relate the electrical conductivity of an electrolyte to the velocity of its ions in an electrical field. To compute the electrical conductance, it is sufficient to calculate

the number of ions passing through any cross section of a vessel with an electrolyte in a unit of time in standard conditions, i.e. at a field intensity equal to 1 V/cm. Since electricity is carried by ions of various signs moving in opposite directions, the total quantity of electricity passing through a solution per second, i.e. the current intensity $I$, is the sum of the quantities of electricity carried respectively by the cations $I_+$ and the anions $I_-$, namely,

$$I = I_+ + I_- \tag{17.4}$$

Let us denote the velocity of the cations by $u'$ (cm/s), the velocity of the anions by $v'$ (cm/s), the equivalent concentration of the ions by $c_i$ (g-eq/cm$^3$), the cross section of the cylindrical vessel by $A$ (cm$^2$), the distance between the electrodes by $l$ (cm) and the potential difference between electrodes by $E$ (V). Let us calculate the quantity of ions passing through a cross section of the electrolyte per second. During this time all the cations that at the initial moment were at a distance of not over $u'$ cm from the selected cross section will pass through it in one direction, i.e. all the cations in the volume $u'A$. The number of cations $n_+$ passing through the cross section per second:

$$n_+ = u'Ac_+$$

Since each gramme-equivalent of ions carries, according to Faraday's law, $F = 96\,487$ C of electricity, the current intensity (in amperes) is

$$I_+ = n_+F = u'Ac_+F$$

Reasoning in a similar way for anions whose velocity is equal to $v'$, we get

$$I_- = v'Ac_-F$$

For the total current intensity (the equivalent concentrations of the ions are the same, i.e. $c_+ = c_- = c_i$):

$$I = I_+ + I_- = (u' + v')\,Ac_iF \tag{17.5}$$

The velocities $u'$ and $v'$ of the ions depend on their nature, the field intensity $E/l$, the concentration, temperature, viscosity of the medium, etc.

Let all the factors except the field intensity be constant, and the velocity of the ions be constant in time when the force applied is constant if the medium in which they move has a sufficient viscosity. Consequently it can be considered that the velocity of the ions is proportional to the applied force, i.e. to the field intensity:

$$u' = u\frac{E}{l} \quad \text{and} \quad v' = v\frac{E}{l} \tag{17.6}$$

where $u$ and $v$ are proportionality factors equal to the velocities of the ions at a field intensity of 1 V/cm. The quantities $u$ and $v$ are called *absolute mobilities* of ions. They are measured in cm$^2$/s·V.

Inserting Eqs. (17.6) into Eq. (17.5), we get

$$I = \frac{(u+v)\, c_i AFE}{l} \tag{17.7}$$

According to Ohm's law

$$I = \frac{E}{R} = EG \tag{17.8}$$

Inserting into Eq. (17.8) the values of $G$ from Eqs. (17.1) and (17.2) and equating the right-hand parts of Eqs. (17.7) and (17.8), we have

$$I = E\frac{\varkappa A}{l} = E\frac{\Lambda c}{1000l} = (u+v)\frac{Fc_i AE}{l} \tag{17.9}$$

Solving Eq. (17.9) with respect to $\Lambda$, we get

$$\Lambda = (u+v)\, F\, \frac{c_i 1000}{c} \tag{17.10}$$

For strong electrolytes whose dissociation is considered complete, the ratio $1000c_i/c = 1$; for weak electrolytes $1000c_i/c = \alpha$. Let us introduce the new symbols

$$U = uF \text{ and } V = vF \tag{17.11}$$

and call the quantities $U$ and $V$ the *mobilities* of ions. Hence for strong electrolytes

$$\Lambda = U + V \tag{17.12}$$

and for weak electrolytes

$$\Lambda = (U + V)\,\alpha \tag{17.13}$$

At infinite dilution (i.e. at $\varphi \to \infty$, $U \to U_\infty$, $V \to V_\infty$ and $\alpha \to 1$) we get

$$\Lambda_\infty = U_\infty + V_\infty \tag{17.14}$$

both for strong and for weak electrolytes. The quantities $U_\infty$ and $V_\infty$ are obviously the *limiting mobilities of ions.* They are equal to the equivalent conductivities of a cation and anion separately at infinite dilution and are measured in the same units as $\Lambda$ or $\Lambda_\infty$, i.e. in $cm^2/\Omega \cdot$g-eq. Equation (17.14) is an expression of *Kohlrausch's law*, which states that *the equivalent conductivity at infinite dilution is equal to the sum of the limiting mobilities of the ions.*

The mobilities $U$ and $V$ in Eq. (17.13) depend on the concentration (dilution) especially for strong electrolytes, where at high concentrations the values of $U$ and $V$ are less than $U_\infty$ and $V_\infty$ owing to mutual affinity of ions of different signs (the influence of the ionic atmosphere). The same is also true for weak electrolytes, but to a smaller extent, since the concentration of the ions there is low.

It should be remembered that the quantities $U$ and $V$ (and, consequently, $U_\infty$ and $V_\infty$) relate to 1 g-eq of the given ions.

Mobility is a most important characteristic of ions reflecting their specific participation in the electrical conductance of an electrolyte.

In aqueous solutions all ions, except for the ions $H_3O^+$ and $OH^-$, have like values of their mobilities. This means that the absolute mobilities of the ions ($u$ and $v$) are also similar, equal to several centimetres per hour (2.5 cm/h for $K^+$, 4.16 for $OH^-$, and 10 for $H_3O^+$).

If the ions are coloured, their movement can be measured directly in certain conditions, and the absolute mobilities can thus be determined.

Using a table of the limiting mobilities of ions (Table 17.2) and Kohlrausch's law, we can easily calculate the limiting conductivity of the corresponding solutions [by Eq. (17.14)].

The equivalent conductivity of solutions of salts is expressed by values of the order of 100-130 $cm^2/g\text{-}eq \cdot \Omega$. Owing to the exceedingly great mobility of hydroxonium ions, the value of $\Lambda_\infty$ for acids is three to four times greater than that for salts. Alkalies occupy an intermediate position.

The motion of an ion can be likened to that of a macroscopic sphere in a viscous medium, and the Stokes formula may be applied in this case:

$$u = \frac{zeE/l}{6\pi r\eta} \tag{17.15}$$

where $e$ = charge of an electron
$z$ = number of elementary charges of an ion (charge number)
$r$ = effective radius of ion
$\eta$ = viscosity factor
$E/l$ = field intensity.

When calculating absolute mobilities, the motive force—the field intensity $E/l$—is taken equal to unity. Consequently, the velocity of ions is inversely proportional to their radius. Let us consider the series $Li^+$, $Na^+$, $K^+$. Since in this series the true radii of ions increase, the mobilities should decrease in the same sequence. In actual conditions this is not true, however. It can be seen from Table 17.2 that the mobilities almost double when passing from $Li^+$ to $K^+$. Hence the conclusion can be reached that ions have different radii in a solution and in an ionic lattice. The smaller the true "crystallochemical" radius of an ion, the greater is its effective radius in an electrolyte. This phenomenon can be explained by the fact that ions in a solution are not free, but are hydrated or, in the general case, solvated. Consequently the effective radius of an ion moving in an electric field will be mainly determined by the degree of its hydration, i.e. by the number of molecules of water bound to the ion.

TABLE 17.2

**Limiting Mobilities of Ions in Water at 25 °C**

| Ion | $U_\infty$ | Ion | $U_\infty$ | Ion | $V_\infty$ | Ion | $V_\infty$ |
|---|---|---|---|---|---|---|---|
| $H_3O^+$ | 349.8 | $Ba^{2+}$ | 63.6 | $OH^-$ | 197.6 | $CNCH_2CO_2^-$ | 41.8 |
| $Li^+$ | 38.6 | $Cu^{2+}$ | 56.6 | $F^-$ | 55.4 | $C_2H_5CO_2^-$ | 35.8 |
| $Na^+$ | 50.1 | $Zn^{2+}$ | 52.8 | $Cl^-$ | 76.4 | $C_3H_7CO_2^-$ | 35.1 |
| $K^+$ | 73.5 | $Cd^{2+}$ | 54.0 | $Br^-$ | 78.1 | $C_6H_5CO_2^-$ | 32.3 |
| $Rb^+$ | 77.8 | $La^{3+}$ | 69.7 | $I^-$ | 76.8 | $SO_4^{2-}$ | 80.0 |
| $Cs^+$ | 77.2 | $Ce^{3+}$ | 69.8 | $N_3^-$ | 69.0 | $C_2O_4^{2-}$ | 74.1 |
| $Ag^+$ | 61.9 | $Pr^{3+}$ | 69.6 | $NO_3^-$ | 71.4 | $CO_3^{2-}$ | 69.3 |
| $Tl^+$ | 74.7 | $Nd^{3+}$ | 69.4 | $ClO_3^-$ | 64.6 | $Fe(CN)_6^{3-}$ | 99.1 |
| $NH_4^+$ | 73.5 | $Sm^{3+}$ | 68.5 | $BrO_3^-$ | 55.8 | $P_3O_9^{3-}$ | 83.6 |
| $CH_3NH_3^+$ | 58.7 | $Eu^{3+}$ | 67.8 | $ClO_4^-$ | 67.3 | $Fe(CN)_6^{4-}$ | 111 |
| $(CH_3)_2NH_2^+$ | 61.8 | $Gd^{3+}$ | 67.3 | $IO_4^-$ | 54.5 | $P_4O_{12}^{4-}$ | 93.7 |
| $(CH_3)_3NH^+$ | 47.2 | $Al^{3+}$ | 63.0 | $ReO_4^-$ | 54.9 | $P_2O_7^{4-}$ | 95.9 |
| $N(CH_3)_4^+$ | 44.9 | $Dy^{3+}$ | 65.6 | $HCO_3^-$ | 44.5 | $P_3O_{10}^{5-}$ | 109 |
| $N(C_2H_5)_4^+$ | 32.6 | $Ho^{3+}$ | 66.3 | $HCO_2^-$ | 54.6 | $[Co(NH_3)_6]^{3+}$ | 101.9 |
| $N(C_3H_7)_4^+$ | 23.5 | $Er^{3+}$ | 65.9 | $CH_3CO_2^-$ | 40.9 | $[CO_2(tri\text{-}en)_3]^{6+}$ [1] | 68.7 |
| $N(C_4H_9)_4^+$ | 19.4 | $Tm^{3+}$ | 65.4 | | | | |
| $N(C_5H_{11})_4^+$ | 17.4 | $Yb^{3+}$ | 65.6 | | | | |
| $Be^{2+}$ | 45.0 | $Co^{2+}$ | 49 | | | | |
| $Mg^{2+}$ | 53.0 | $Fe^{2+}$ | 53.5 | | | | |
| $Ca^{2+}$ | 59.5 | $Fe^{3+}$ | 68.0 | | | | |
| $Sr^{2+}$ | 59.5 | | | | | | |

[1] Tri-en is an abbreviation for triethylenetetramine; the capacity of this ligand is four, the coordination number of trivalent cobalt is six.

The bond of an ion with solvent molecules, in particular with molecules of water, is an ionic-dipole one. The field intensity on the surface of a lithium ion is much greater than on that of a potassium ion (since the surface of the former is less than that of the latter, and the radius, i.e. the distance from the water dipoles to the effective point charge at the centre of the ion, is smaller). Consequently the degree of hydration of a lithium ion is greater than that of a potassium ion. According to the Stokes formula, multiple-charge ions should have a greater mobility than single-charge ones. A glance at Table 17.2 shows that the velocities of multiple-charge ions differ quite little from those of single-charge ones, which is obviously explained by the greater degree of their hydration owing to the greater strength of the field created by multiple-charge ions.

It should be remembered that the applicability of the Stokes formula to separate ions is insufficiently substantiated. The Stokes formula describes the motion of a sphere in a continuous medium. The solvent is not such a medium for the ions. For this reason all the conclusions ensuing from the Stokes formula and relating to the hydration of ions have only a qualitative nature, and apparently can be applied for a quantitative appraisal of the motion of only large spherical ions of the type $N(C_4H_9)_4^+$.

**17.4. Mobility of Hydroxonium and Hydroxyl Ions.** The unusually high mobilities of hydroxonium and hydroxyl ions were noted a long time ago.

It was previously considered that an aqueous solution contains hydrogen ions whose high velocity is explained by their exceedingly small radius. The groundlessness of this assumption became obvious after it was established that a solution contains not hydrogen ions ($H^+$), but hydroxonium ions ($H_3O^+$). These ions, like hydroxyl ions, are hydrated and their effective radii have the same order as the radii of other ions. Consequently, if the mechanism by which these ions carry electricity were the usual one, their mobility would also not differ appreciably from those of other ions. This is what is actually observed in most non-aqueous solutions. An anomalously high mobility of $H_3O^+$ and $OH^-$ manifests itself only in aqueous solutions and in the simplest alcohols. This is obviously due to the features of the carrying of electricity by these ions, which differ from other ions in that they are ions of the solvent itself—water or the simplest alcohols.

It is known that the process of dissociation of water proceeds as follows:

$$H_2O + H_2O = OH^- + H_3O^+$$
$$H^+$$

and consists in the transition of a proton from one molecule of water to another one. The hydroxonium ions formed continuously and chaotically exchange protons with the surrounding molecules of water. When a potential difference is created, however, a directed motion appears in addition to a random one. Part of the protons begin to move along the lines of force of the field toward the cathode and, consequently, carry electricity.

Thus, electricity is mainly carried not by hydroxonium ions, although they do participate in the carrying of electricity, but by protons migrating from one molecule of water to another one in oriented motion, along the lines of force of the field. Account must also be taken of the necessity of rotation of the newly formed molecule of water, which immediately after the migration of a proton

has an orientation that does not permit it to accept, in turn, a proton from the right from another hydroxonium ion.

This motion of the protons increases the electrical conductance of a solution, because the protons have a very small radius and do not travel the entire distance to the cathode, but only the distances between water molecules. This type of conductance can be called *relay* or *chain* conductance[1].

The high mobility of hydroxyl ions can be explained in a similar way, except that in this case the protons migrate not from the hydroxonium ions to the molecules of water, but from the latter to the hydroxyl ions. This leads to the apparent motion of the hydroxyl ions toward the anode.

Hydroxyl ions actually do appear in the anode space, but this is mainly explained not by their motion, but by migration of the protons in the direction of the cathode.

If the numbers of $H_3O^+$ and $OH^-$ ions are the same, the number of proton migrations according to the scheme $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$ will be greater than the number of migrations according to the scheme $H_2O + HO^- \rightarrow OH^- + H_2O$, since the energy state of hydrogen in a water molecule corresponds to a deeper minimum of the potential energy (a *potential trough*) than in an $H_3O^+$ ion. This explains the lower mobility of a hydroxyl ion.

Naturally, the ions $H_3O^+$ and $OH^-$ as such also move when a potential difference is created between the electrodes and carry electricity, but their contribution to electrical conductance is probably about the same as that of other ions. The high electrical conductance of acids and bases is explained by the chain mechanism of electrical conductance with the participation of protons.

**17.5. Relation between Mobility of Ions and Their Concentration.** Arrhenius's theory of electrolytic dissociation did not take into account the influence of concentration on ionic mobility, although it has been established that this influence may be quite appreciable. Arrhenius explained the reduction in the equivalent conductivity with the concentration not by a decrease in ionic mobility, but by a decrease in the degree of dissociation.

As indicated above, Kohlrausch deduced an empirical equation relating the equivalent conductivity of strong electrolytes to the concentration, i.e. $\Lambda = \Lambda_\infty - A\sqrt{c}$.

Since $\Lambda_\infty = U_\infty + V_\infty$ and $\Lambda = U + V$, therefore,

$$U = U_\infty - B_1\sqrt{c} \quad \text{and} \quad V = V_\infty - B_2\sqrt{c} \qquad (17.16)$$

where $B_1 + B_2 = A$.

[1] This explanation is probable, but not indisputable. It is possible that whole groups of associated molecules (so-called "swarms") participate in the migration of a proton.

P. Debye and E. Hückel explained the reduction in ionic mobility and in the equivalent conductivity $\Lambda$ of strong electrolytes with a growth in the concentration by the presence of an ionic atmosphere. Indeed, every ion is surrounded by an ionic atmosphere consisting mainly of ions having a sign opposite to that of the central one. The density of the atmosphere increases with a growth in the concentration of the electrolyte.

When an electric field is applied, an ion begins to migrate in one direction, and its ionic atmosphere in the opposite one. This motion of ions having different charges in opposite directions creates, as it were, additional friction, and it is the latter that decreases the absolute velocity of the ions. This phenomenon is called the *electrophoretic effect.* A growth in the concentration is accompanied by an increase in the density of the ionic atmosphere. Hence the retarding electrophoretic effect also grows.

It should not be thought that in the random motion of an ion its ionic atmosphere moves together with it as a single whole. In migration, an ion leaves its ionic atmosphere and along its path continuously creates a new one. Although this process of destruction and creation of the ion atmosphere proceeds rapidly, it is not instantaneous. The result is that the symmetry of the ionic atmosphere is violated, its density being greater behind the moving ion than ahead of it. The asymmetry of the ionic atmosphere obviously also results in a certain retardation of the translational movement of an ion. This phenomenon is called the *relaxation* or *asymmetry effect.* Thus, owing to the presence of an ionic atmosphere, two retardation effects appear in the motion of an ion, namely, the electrophoretic effect due to movement of the ionic atmosphere in a direction opposite to that of motion of an ion, and the asymmetry effect due to asymmetry of the ionic atmosphere.

A convincing confirmation of the truth of Debye's and Hückel's ideas is the so-called Wien effect discovered in 1927. If the decrease in ionic mobility with a growth in concentration is explained by the presence of an ionic atmosphere, then destroying of the latter should lead to a growth of mobility and, consequently, of electrical conductivity to its limiting value. The velocity of an ion is proportional to the field strength and the rate of formation of an ionic atmosphere is a finite quantity. It is therefore obvious that by increasing the field strength such a high velocity of the ions can be achieved at which the ionic atmosphere no longer has time to form. In this case the ions will leave their ionic atmospheres (which immediately become destroyed) and move without them. The ions will therefore have the maximum velocity and mobility. It is this phenomenon that was established by M. Wien. By increasing the field strength to 200 000 V/cm, he observed an increase in the equivalent conductivity to the limiting value $\Lambda_\infty$.

It is interesting to note that in weak electrolytes the Wien effect was found to be much greater than in strong ones. This points to an increase in the degree of dissociaton of the dissolved molecules under the influence of an electric field having a high strength.

In 1928 P. Debye and H. Falkenhagen theoretically considered the influence of the frequency of an alternating current on the electrical conductivity of electrolytes. They established that when the frequency grows to above a certain value, an appreciable increase in the conductivity should be observed. This phenomenon was called the *frequency* or *Debye-Falkenhagen effect*, or *dispersion of electrical conductivity*. It was experimentally confirmed by a number of investigators.

Debye and Falkenhagen found that at a sufficiently great frequency of an alternating current, the mutual displacements of an ion and the ionic atmosphere are so small that the latter is practically symmetrical, and for this reason the retarding asymmetry effect due to asymmetry of the ionic atmosphere should vanish. The relaxation time $\theta$ of an ionic atmosphere is the time in which the ionic atmosphere vanishes after removal of the central ion (and, obviously, in which it again forms around an ion appearing at a new point). According to the Debye-Falkenhagen theory, the quantity $\theta$ (in seconds) is determined by the equation

$$\theta = \frac{71.3 \times 10^{-10}}{c\Lambda z}$$

where $c$ is the concentration in g-eq/dm$^3$.

The frequency $\nu$ of an alternating current at which a growth of the electrical conductivity can be expected is the reciprocal of the relaxation time, namely,

$$\nu = \frac{1}{\theta} = \frac{cz\Lambda}{71.3} \times 10^{10}$$

For solutions of mono-monovalent salts at $c = 0.001$ the Debye-Falkenhagen effect manifests itself at a frequency of $10^9$ Hz. At higher frequencies the asymmetry effect vanishes. The electrophoretic effect remains, since the ionic atmosphere is not destroyed.

Consequently, the Debye-Falkenhagen effect should be weaker than the Wien effect. By comparing their values, we can divide the total effect of the decrease in electrical conductivity into components due to electrophoretic and asymmetry effects. Indeed, the Wien effect appears at complete disappearance of the ionic atmosphere and, consequently, of both retardation effects. The Debye-Falkenhagen effect is explained only by disapperance of symmetry of the ionic atmosphere. Experiments show that the latter effect is about one-third of the Wien effect, i.e. the electrophoretic effect is two times greater than the asymmetry effect.

The experiments of Wien and of Debye and Falkenhagen are a convincing proof of the real existence of an ionic atmosphere and make it possible to form an idea of the nature of its structure. The conception of an ionic atmosphere is one of the fundamental tenets of the electrostatic theory of electrolytes.

L. Onsager developed these ideas and deduced a theoretical equation that quantitatively relates the equivalent electrical conductivity to the concentration and makes it possible to calculate the electrophoretic and the asymmetry effects. For binary monovalent aqueous electrolytes the Onsager equation has the form

$$\Lambda' = \Lambda_\infty - \left[\frac{8.2\times10^5}{(\varepsilon_r T)^{3/2}}\Lambda_\infty + \frac{82.4}{(\varepsilon_r T)^{1/2}\eta}\right]\sqrt{c'} \qquad (17.17)$$

where $\varepsilon_r$ = relative permittivity
$\eta$ = viscosity coefficient
$T$ = temperature
$c'$ = concentration.

The addend $\frac{8.2\times10^5\Lambda_\infty}{(\varepsilon_r T)^{3/2}}\sqrt{c'}$ characterizes the asymmetry effect, and the addend $\frac{82.4}{(\varepsilon_r T)^{1/2}\eta}\sqrt{c'}$ the electrophoretic effect.

Onsager's theoretical equation agrees with Kohlrausch's empirical formula ($\Lambda = \Lambda_\infty - A\sqrt{c}$) at moderate concentrations, which is an appreciable argument in favour of the electrostatic theory of electrolytes.

**17.6. Temperature Dependence of Ionic Mobility.** The limiting mobilities of ions, and also the conductivity of electrolytes always increase with a growth in the temperature (in contrast to the electrical conductivity of metals, which decreases with a growth in the temperature). The values of the limiting mobilities at various temperatures are given in Table 17.3.

The temperature coefficient of mobility $\frac{1}{u_{291}}\cdot\frac{\Delta U}{\Delta T}$ is quite great (about 0.02). When a solution is heated by one kelvin, the mobility and, therefore, the conductivity grow by approximately 2%, which makes it necessary to use thermostats for accurate measurement of the electrical conductivity. The greatest temperature coefficient is characteristic of ions with a relatively low mobility and vice versa. The positive temperature coefficient of ionic mobility is apparently explained by the reduction in viscosity with a growth in temperature.

If this is true, then on the basis of the Stokes formula (17.15) we can reach the conclusion that

$$U\eta = \frac{ze}{6\pi r} = \text{const} \qquad (17.18)$$

i.e. the product of the mobility (and, consequently, of the conductivity) and the viscosity coefficient is a constant quantity. For this reason the temperature coefficient of mobility should be equal to a quantity that is the reciprocal of the temperature coefficient of viscosity. Indeed, the temperature coefficient of mobility for most ions in aqueous solutions is equal to 0.023-0.025, while the quantity that is the reciprocal of the temperature coefficient of viscosity of water is equal

TABLE 17.3

**Limiting Mobilities of Ions in Water at Various Temperatures**

| Ion | Limiting mobility at temperature of | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0 °C | 5 °C | 15 °C | 18 °C | 25 °C | 35 °C | 45 °C | 55 °C | 100 °C |
| $H_3O^+$ | 225 | 250.1 | 300.6 | 315 | 349.8 | 397.0 | 441.4 | 483.1 | 650.0 |
| $OH^-$ | 105 | — | — | 171 | 197.6 | — | — | — | 450.0 |
| $Li^+$ | 19.4 | 22.7 | 30.2 | 32.8 | 38.6 | $48.0_0$ | 58.0 | 68.7 | 115.0 |
| $Na^+$ | 26.4 | 30.0 | 39.7 | 42.8 | 50.1 | $61.5_4$ | 73.7 | 86.9 | 145.0 |
| $K^+$ | 40.7 | 46.7 | 59.6 | 63.9 | 73.5 | $88.2_1$ | 103.5 | 119.2 | 195.0 |
| $Rb^+$ | 43.9 | 50.1 | 63.4 | 66.5 | 77.8 | $92.9_1$ | 108.5 | 124.2 | — |
| $Cs^+$ | 44.0 | 50.0 | 63.1 | 67 | 77.2 | $92.1_0$ | 107.5 | 123.6 | — |
| $Ag^+$ | 33.1 | — | — | 53.5 | 61.9 | — | — | — | 175.0 |
| $NH_4^+$ | 40.2 | — | — | 63.9 | 73.5 | — | — | — | 180.0 |
| $N(CH_3)_4^+$ | 24.1 | — | — | 40.0 | 44.9 | — | — | — | — |
| $N(C_2H_5)_4^+$ | 16.4 | — | — | 28.2 | 32.6 | — | — | — | — |
| $N(C_3H_7)_4^+$ | 11.5 | — | — | 20.9 | 23.4 | — | — | — | — |
| $N(C_4H_9)_4^+$ | 9.6 | — | — | — | 19.4 | — | — | — | — |
| $N(C_5H_{11})_4^+$ | 8.8 | — | — | — | 17.4 | — | — | — | — |
| $Mg^{2+}$ | 28.9 | — | — | 44.9 | $53.0_5$ | — | — | — | 165 |
| $Ca^{2+}$ | 31.2 | — | 46.9 | 50.7 | 59.50 | 73.2 | 88.2 | — | 180 |
| $Sr^{2+}$ | 31 | — | — | 50.9 | $59.4_5$ | — | — | — | — |
| $Ba^{2+}$ | 34.0 | — | — | 54.6 | $63.6_3$ | — | — | — | 195 |
| $Cd^{2+}$ | — | — | — | 44.8 | 54.0 | — | — | — | — |
| $La^{3+}$ | 34.4 | — | — | 59.5 | 69.7 | — | — | — | 215 |
| $NO_3^-$ | 40.0 | — | — | 62.3 | 71.44 | — | — | — | 195 |
| $ClO_4^-$ | 36.9 | — | — | 58.8 | 67.3 | — | — | — | 185 |
| $CH_3CO_2^-$ | 20.1 | — | — | 35.0 | $40.9_0$ | — | — | — | — |
| $F^-$ | — | — | — | 47.3 | 55.4 | — | — | — | — |
| $Cl^-$ | 41.0 | 47.5 | 61.4 | 66.0 | 76.4 | 92.2 | 108.9 | 126.4 | 212.0 |
| $Br^-$ | 46.2 | 49.2 | 63.1 | 68.0 | 78.1 | 94.1 | 110.7 | 127.8 | — |
| $I^-$ | 41.4 | 48.5 | 62.1 | 66.0 | 76.8 | 92.4 | 108.6 | 125.4 | |
| $SO_4^{2-}$ | 41 | — | — | 68.4 | 80.0 | — | — | — | 260 |
| Viscosity of water $\eta_0$, cP | 1.787 | 1.516 | 1.138 | 1.053 | 0.8903 | 0.7194 | 0.5963 | 0.5044 | 0.2829 |

to 0.0243. The applicability of the Stokes law and, therefore, Eq. (17.18), however, should be expected only to ions having a sufficiently great volume (see Sec. 17.9).

The product of the limiting mobility of an ion ($U_0$, $V_0$) and the viscosity $\eta_0$ of the solvent does not practically change within a broad range of temperatures. For example, the product $V_0\eta_0$ is practically constant for acetate ions in an aqueous solution:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $t$, °C . . . . . | 0 | 18 | 25 | 59 | 75 | 100 | 128 | 156 |
| $V_0\eta_0$ . . . . . | 0.366 | 0.368 | 0.366 | 0.368 | 0.369 | 0.369 | 0.369 | 0.369 |

In non-aqueous solutions the product $V_0\eta_0$ (or $U_0\eta_0$) also does not practically change with a change in the temperature, but this law is not always observed completely.

Since $\Lambda_\infty = U_0 + V_0$, the equivalent conductivity at infinite dilution always grows with the temperature.

A more complicated relation exists between the equivalent conductivity and the mobility for a finite concentration. For a weak electrolyte $\Lambda = (U + V)\,\alpha$. If the mobilities of ions increase with the temperature, the degree of dissociation may decrease, because the relative permittivity of a solution reduces upon heating, i.e. the forces of interaction between the ions grow. Therefore the curve showing the temperature dependence of the conductivity may have a maximum.

A similar phenomenon is also observed in strong electrolytes, since heating not only increases the mobility of the ions owing to a reduction in the viscosity, but also reduces the relative permittivity. This results in an increase in the density of the ionic atmosphere and, hence, in greater electrophoretic and asymmetry effects.

**17.7*. Conductance of Non-Aqueous Solutions.** Not only aqueous, but also non-aqueous solutions may conduct electricity. The conductance of non-aqueous solutions is also determined by the concentration of the ions and their velocity, but the specific properties of the solvent display themselves very sharply.

The conductivity of non-aqueous solutions is usually much lower than that of their aqueous counterparts. An exception are ammonia solutions, and also solutions in HCN, where the conductivity is much higher than in aqueous ones. Table 17.4 gives the values of the conductivity of solutions of HCl in various solvents, and also the relative permittivities of these solvents.

TABLE 17.4

**Maximum Equivalent Conductivity $\Lambda_{max}$ of HCl Solutions and Relative Permittivity $\varepsilon_r$ of Solvents**

| Solvent | $\varepsilon_r$ | $\Lambda_{max}$ | Dilution at $\Lambda_{max}$, dm³/g-eq |
|---|---|---|---|
| $H_2O$ | 81 | 394 | — |
| $CH_3OH$ | 31.2 | 117.06 | 97.16 |
| $C_2H_5OH$ | 25.8 | 27.17 | 100 |
| $C_3H_7OH$ | 22.2 | 9.74 | 35.47 |
| *iso*-$C_4H_9OH$ | 28.2 | 4.00 | 136.3 |
| *iso*-$C_5H_{11}OH$ | — | 2.6 | 1.9 |
| $(C_2H_5)_2O$ | 4.37 | 0.0439 | 3.52 |

The conductivity of a solution of HCl in methyl alcohol is approximately one-fourth of that in water, which is difficult to explain by the reduction in the velocity of the ions. The low conductivity in non-aqueous media is mainly determined by the low degree of dissociation of substances in these solvents. Thus, if hydrogen chloride dissociates completely in an aqueous solution, its degree of dissociation in an alcohol solution is much smaller than unity, and in benzene it forms a very weak electrolyte.

The first investigations of the conductance of non-aqueous solutions were conducted by R. Lents (1878-1882) and I. Kablukov (1889). Kablukov showed that there is a parallelism between the electrical conductance of a solution and the relative permittivity of the solvent. This law, known as the Thomson-Nernst law [though the latter, independently of each other, indicated not this relation, but that between the dissociation and the relative permittivity of the solvent (1893, 1894)] is illustrated by Table 17.4.

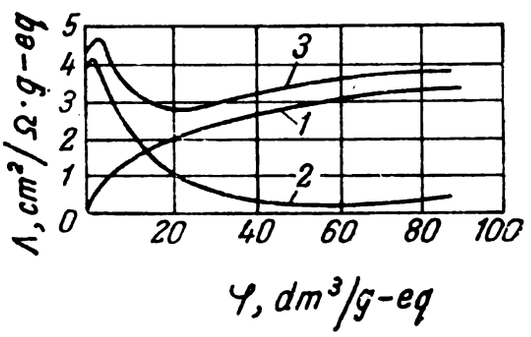



Fig. 17.5. Dependence of equivalent conductivity of $AgNO_3$ solutions in pyridine on dilution

The influence of the relative permittivity on the degree of dissociation of a substance should naturally be considerable, since the permittivity determines the force of Coulombian interaction between the ions formed $f = \frac{e_1 e_2}{\varepsilon_r r^2}$.

It is quite clear that the greater the electrostatic interaction between ions, the smaller should the degree of dissociation be. But the permittivity cannot be considered as the sole factor affecting electrolytic dissociation, since in the majority of cases dissociation is a complex function of specific properties of both the solvent and the solute, and also a function of their interaction.

The insufficiently general nature of the Kablukov-Thomson-Nernst law, which does not take into consideration the specific nature of the solute, is obvious. This can be shown, for example, by the fact that some substances dissociate completely (HCl) and others very poorly ($CH_3COOH$) in the same solvent having a quite definite relative permittivity (for example, in water). Frequently a considerable conductivity of a solution is observed at a low value of the relative permittivity of the solvent. The dependence of the conductivity of non-aqueous solutions of electrolytes on the concentration is often of a complicated nature. The so-called *anomalous conductivity* is observed. This was first discovered by Kablukov for a solution of $AgNO_3$ in pyridine, whose equivalent conductivity when plotted against the dilution (Fig. 17.5) has a minimum. The simplest explanation of curves having a minimum was given by A. Sakhanov. A solution of $AgNO_3$ in pyridine has double molecules $(AgNO_3)_2$ which greatly dissociate into complex ions. Upon dilution the dimer molecules decompose into simple $AgNO_3$ ones that dissociate poorly (curve *2*). As dilution is continued, however, the $AgNO_3$ nevertheless dissociates into $Ag^+$ and $NO_3^-$, and the conductivity of these ions grows (curve *1*). The total conductivity of all the ions has a minimum (curve *3*).

When bromine is dissolved in pyridine, the complex compound $C_5H_5NBr_2$ is formed. It dissociates according to the scheme

$$C_5H_5NBr_2 \rightleftharpoons C_5H_5NBr^+ + Br^-$$

The equivalent conductivity of solutions of KI in liquid sulphur dioxide and of $(C_3H_7)_4NI$ in dichloromethane changes in a more complicated way. The curve showing the dependence of the equivalent conductivity of these solutions on the concentration has both a maximum and a minimum.

P. Walden found a rule that relates the concentration of a non-aqueous electrolyte $c_{min}$ corresponding to the minimum of its equivalent conductivity and the relative permittivity of the medium $\varepsilon_r$ and can be written as follows:

$$c_{min} = C\varepsilon_r^3 \tag{17.19}$$

Where $C$ is a coefficient that is constant for a given substance dissolved in various solvents.

The formation of complex ions when the relative permittivity of the solvent decreases can be observed qualitatively during the heating of concentrated aqueous solutions of $CoCl_2$. Their pink colour is due to the presence of the ion $Co^{2+}$. Heating of the solution reduces the relative permittivity of the water, which facilitates the formation of complex ions, namely,

$$2Co^{2+} + 4Cl^- \longrightarrow Co^{2+} + [CoCl_4]^{2-}$$

which imparts a blue colour to the solution. When the solution is cooled it again acquires a pink colour.

Much was done by V. Plotnikov and his pupils for understanding the molecular structure of non-aqueous electrolytes and the nature of their conductance. They developed the notions of dissociating complexes set out above, which were confirmed by the results of further investigations. Many complexes were synthesized and studied that were found to be definite coordination compounds. In many cases complexes are unstable formations with a structure that is still unknown. The formation of ionic pairs and triplets also plays a part in anomalous conductivity.

Thus non-aqueous electrolytes have the features indicated above, but the main laws holding for aqueous solutions can be also applied to non-aqueous ones (for example, Faraday's law, Kohlrausch's equation).

**17.8*. Ionic Mobility in Non-Aqueous Solutions.** The influence of a solvent on ionic mobility is illustrated by Table 17.5, from which it follows that ionic mobilities in organic solvents are of the same order as in aqueous solutions, i.e. they are expressed by values equal to scores of mhos (reciprocal ohms). The mobilities of ions may change several times depending on the solvent. The mobilities are frequently less in non-aqueous solutions than in aqueous ones. Exceptions to the rule are encountered, however. For example, for solutions in acetone and hydrogen cyanide the influence of the solvent on ionic mobility can be related to the viscosity of the solvent. Hence, applying the Stokes formula to the motion of an ion in a dilute solution, we get

$$U_0 = \frac{ze}{6\pi r \eta_0} \tag{17.20}$$

where $\eta_0$ is the viscosity of the solvent.

It can be assumed that the product of the mobility and, therefore, the equivalent conductivity and the viscosity do not depend on the nature of the solvent and is a constant quantity (on condition that the radius of an ion also remains constant):

$$U_0\eta_0 = \frac{ze}{6\pi r} = \text{const} \tag{17.21}$$

This law is similar to the one indicated above (see Sec. 17.6), but there we established the independence of the product on the temperature in one solvent, and here on the nature of the solvent at a constant temperature.

Equation (17.21) is called *Walden's rule* (1906), although similar laws were proposed still earlier by S. Arrhenius and L. Pisarzhevsky.

In the majority of cases this rule cannot be used to interprete the influence of the solvent, although it is this influence that it was designed to reflect. Thus, at

TABLE 17.5

**Limiting Mobilities of Ions in Selected Solvents at 25 °C**

| Ion | Limiting mobilities in | | | | |
|---|---|---|---|---|---|
| | water | methyl alcohol | ethyl alcohol | acetone | nitrobenzene |
| $H^+$ | 349.8 | 143 | 59.5 | 88.0 | 23 |
| $Li^+$ | 38.6 | 39.8 | | | |
| $Na^+$ | 50.1 | 45.2 | 18.7 | 80.0 | 17.2 |
| $K^+$ | 73.5 | 52.4 | 22.0 | 82.0 | 19.2 |
| $NH_4^+$ | 73.5 | 57.9 | 19.3 | 98.0 | |
| $Ag^+$ | 61.9 | 50.3 | 17.5 | 88.0 | 18.5 |
| $Cl^-$ | 76.4 | 52.9 | 24.3 | 111.0 | 17.3 |
| $Br^-$ | 78.1 | 55.5 | 25.8 | 113.0 | 19.6 |
| $I^-$ | 76.8 | 62.7 | | | |
| $ClO_4^-$ | 67.3 | 70.9 | 33.8 | 117.0 | 19.9 |
| $NO_3^-$ | 71.4 | 60.8 | 27.9 | 120.0 | — |
| $OH^-$ | 197.6 | 53.0 | 22.5 | | |
| $CNS^-$ | 66.5 | 61.0 | 29.2 | 123.0 | — |

20 °C the viscosity of methyl alcohol is about one-half of that of pure water (0.58 and 1.005). An increase in ionic mobility of about two times should have been expected when passing over from an aqueous solution to an alcohol one. In practice this assumption was not confirmed, however, and the values of the mobilities were found to be almost the same (43.5 and 45.8 for a sodium ion, 54.4 and 50.3 for a silver ion, and 65.5 and 51.3 for a chloride ion).

At 20 °C the viscosity of ethyl alcohol (1.19 cP) only slightly differs from that of water (1.005 cP), although the mobilities of the ions in ethyl alcohol are one-half to one-third of those in water. The viscosity of acetone (0.32 cP) is about one-third of that of water, while the mobility of ions when passing over from water to acetone grows to a much smaller extent.

The fact that Walden's rule is not observed when comparing various solvents is obvious and can easily be explained. It postulates the equality of the effective radii of the ions in different solvents, which is not only difficult to substantiate, but also even to imagine. It is this lack of observance of Walden's rule that convincingly points to ions being solvated to a different extent in different solvents. By using the Stokes equation, attempts were made to determine the effective radius of an ion according to the value of the mobility, and then to find the degree of solvation. As indicated at the end of Sec. 17.3, the Stokes law is obeyed more accurately for large ions whose dimensions considerably exceed those of the solvent molecules, for example such ions as $N(C_4H_9)_4^+$, $N(C_5H_{11})_4^+$ and picrate ion $C_6H_2(NO_2)_3O^-$. Thus, the following data were obtained for solutions of $(C_2H_5)_4NI$ in various solvents (at 25 °C and above):

| Solvent . . . . | $CH_3OH$ | $CH_3COCH_3$ | $CH_3CN$ | $C_2H_4Cl_2$ | $CH_3NO_2$ | $C_6H_5NO_2$ |
|---|---|---|---|---|---|---|
| $\Lambda_\infty\eta_0$ . . . . . | 0.63 | 0.66 | 0.64 | 0.60 | 0.69 | 0.70 |

The viscosity of the solvent $\eta_0$ is expressed in poises. Thus Walden's rule is confirmed here.

The fact deserves attention that the mobility of hydroxyl ions in all non-aqueous solutions is almost the same as that of other ions. This confirms the assumption that the unusually high mobility of this ion in aqueous solutions is due not to its high velocity, but to the special mechanism of carrying electricity.

The unusually high mobility of hydroxonium ions, though less than in aqueous solutions, is retained in methyl and ethyl alcohols, but is not observed in other solvents. Hence it follows that a solvated proton in non-aqueous solutions carries electricity in the usual way, i.e. by direct motion toward the cathode, and only in alcohol solutions does the proton obtain the possibility of more advantageous motion (a chain or relay mechanism). Apparently ionization (dissociation), for example, of hydrogen chloride in an alcohol solution follows the equation

$$HCl + C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + Cl^-$$

i.e. the ion $C_2H_5OH_2^+$ (ethoxonium) is formed, similar to hydroxonium. This ion can exchange a proton with an alcohol molecule. Thus the possibility of relay conductivity according to the following scheme is possible:

$$C_2H_5OH_2^+ + C_2H_5OH \longrightarrow C_2H_5OH + C_2H_5OH_2^+$$
$$\quad\quad H^+$$

similar to the process in an aqueous medium:

$$H_3O^+ + H_2O \longrightarrow H_2O + H_3O^+$$
$$\quad\quad H^+$$

Consequently, the relatively high conductivity of alcohol solutions in this case is due to the retaining, although to a smaller extent, of chain or relay conductivity as a result of similar structure of molecules of water and alcohol and a considerable affinity of the latter to proton.

**17.9*. Mobility and Hydration Numbers of Ions.** It is clear from the foregoing that the greater the radius of an ion, the more accurately the Stokes law should be observed. On the basis of this assumption we can attempt to introduce corrections to the Stokes formula to appraise more accurately the dimensions of ions in an aqueous solution and, therefore, determine the hydration numbers

TABLE 17.6

**Corrections to the Stokes Formula**

| Ion | $r_c$, Å | $r_S$, Å | $r_c/r_S$ |
|---|---|---|---|
| $N(CH_3)_4^+$ | 3.47 | 2.04 | 1.70 |
| $N(C_2H_5)_4^+$ | 4.00 | 2.81 | 1.42 |
| $N(C_3H_7)_4^+$ | 4.52 | 3.92 | 1.15 |
| $N(C_4H_9)_4^+$ | 4.94 | 4.71 | 1.05 |
| $N(C_5H_{11})_4^+$ | 5.29 | 5.25 | 1 01 |

of ions, i.e. the number of water molecules in the hydration shell of an ion. It can be considered that ions $N(R)_4^+$ (where R is an alkyl radical) are weakly or not at all hydrated, since hydrophobic hydrocarbon groups that react very weakly with the water dipoles are on the surface of these large ions. The radii of ions of this type determined with the aid of the Stokes formula should be equal to those of ions in crystal lattices of the relevant salts. This assumption is confirmed by the fact that for ions of this type the product $\Lambda_\infty \eta_0$ depends neither on the temperature nor on the nature of the solvent.

Table 17.6 compares the values of the crystal radii $r_c$ of ions $N(R)_4^+$ with the values obtained from the Stokes formula ($r_S$). The discrepancy between these values decreases with an increase in the radius of the ion, and for tetrabutyl- and tetraamylammonium it approaches zero (Fig. 17.6).

Let us assume that the difference between the values of $r_c$ and $r_S$ is determined only by the unapplicability of the Stokes formula to small ions. The factor $r_c/r_S = f(r_S)$ can therefore be used as a correction to the radii $r_S$ for hydrated ions found from the Stokes formula. Consequently, the true radius of an ion $r$ is

$$r = \frac{0.820z}{U_0\eta_0}\,\frac{r_c}{r_S}$$

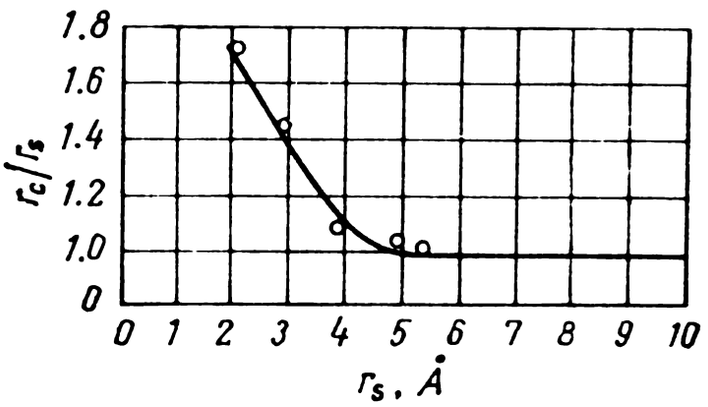



Fig. 17.6. Dependence of correction to the Stokes formula on the radius of ions

The volume of a solvation shell $V_s = \frac{4}{3}\pi r^3 - \frac{4}{3}\pi r_c^3$. Neglecting electrostriction (the compression of water in an electric field) and assuming that the volume of one molecule of water is equal to 30 Å$^3$, we get the following expression for the number of water molecules in a solvation shell:

$$n = \frac{V_s}{30}$$

Table 17.7 gives the hydration numbers of ions calculated in this way.

TABLE 17.7

**Hydration Numbers of Ions Calculated according to the Stokes Formula with a Correction for the Dimensions of an Ion**

| Ion | $U_0$ | $r_S$ | $r$ | $r_c$ | $\frac{4}{3}\pi(r^3 - r_c^3)$, Å | $n$ |
|---|---|---|---|---|---|---|
| $Na^+$ | 50.10 | 1.83 | 3.3 | 0.97 | 150 | 5 |
| $Li^+$ | 36.68 | 2.37 | 3.7 | 0.60 | 210 | 7 |
| $Be^{2+}$ | 45.0 | 4.08 | 4.6 | | 410 | 13-14 |
| $Mg^{2+}$ | 53.05 | 3.46 | 4.4 | 0.65 | 360 | 12 |
| $Ca^{2+}$ | 59.50 | 3.09 | 4.2 | 0.99 | 310 | 10 |
| $Sr^{2+}$ | 59.45 | 3.09 | 4.2 | 1.13 | 310 | 10 |
| $Ba^{2+}$ | 63.63 | 2.88 | 4.1 | 1.35 | 290 | 9-10 |
| $Zn^{2+}$ | 53.0 | 3.46 | 4.4 | 0.74 | 360 | 12 |
| $La^{3+}$ | 69.75 | 3.95 | 4.6 | 1.15 | 410 | 13-14 |

**17.10. Transport Numbers of Ions.** One of the important concepts in electrochemistry is the *transport number of ions* (also called the *transference number* or *migration number*). Electricity is simultaneously carried in electrolytes by positive and negative ions. Hence the question naturally arises as to how ions of each sign participate in this process (for example, the parts played by $Ba^{2+}$ and $Cl^-$ in a solution of $BaCl_2$, or the parts played by $K^+$, $Al^{3+}$ and $SO_4^{2-}$ in a solution of aluminium alum).

The quantity of electricity carried is determined by the concentration and velocity of the ions. Since the concentrations of the cations and anions in a mono-monovalent electrolyte are the same, their contribution to the carrying of electricity obviously depends only on their relative velocity. It is known that the velocities of cations and anions may essentially differ. For this reason their transport numbers should also differ. This was established by J. Hittorf (1854) as a result of investigating the change in the concentration of an electrolyte at the electrodes when a current flowed through it.

By the transport number of an ion is meant the fraction of the total quantity of electricity flowing through an electrolyte carried by the given species of ion. In other words, *the transport number of an ion is the ratio of the quantity of electricity carried by ions of a given species through a cross section of the electrolyte to the total quantity of electricity I that has passed through this section of the electrolyte.*

Let us establish the relation between the transport numbers and the velocities of ions. The fraction of the quantity of electricity carried by an ion is obviously equal to the fraction of the current intensity falling to the given species of ion.

Denoting the quantity of electricity carried by the cations $I_+$, we obtain for the transport number of a cation

$$t_+ = \frac{I^+}{I}$$

Similarly for an anion

$$t_- = \frac{I_-}{I}$$

Since $I_+ + I_- = I$, it is obvious that for a substance decomposing into ions of two species we have

$$t_+ + t_- = \frac{I_+ + I_-}{I} = 1$$

When the potential gradient is not equal to unity ($E/l \neq 1$), we get, similar to the foregoing [see Sec. 17.3 and Eqs. (17.5) and (17.6)]:

$$I_+ = \frac{uqc_+FE}{l} \qquad I_- = \frac{uqc_-FE}{l}$$

$$I = I_+ + I_- = \frac{(u+v)\,qcFE}{l}$$

Hence

$$\left.\begin{aligned} t_+ &= \frac{I_+}{I} = \frac{u}{u+v} = \frac{U}{U+V} \\ t_- &= \frac{I_-}{I} = \frac{v}{u+v} = \frac{V}{U+V} \end{aligned}\right\} \qquad (17.22)$$

*Thus the transport number is equal to the ratio of the velocity (or mobility) of a given ion to the sum of the velocities (or mobilities) of the cation and anion.* Since the mobilities of a cation and an anion change differently with the concentration and temperature in the general case, the transport numbers are also a function of the concentration and temperature. The transport numbers, however, express the ratio of the mobilities, hence their dependence on the concentration and temperature is less appreciable.

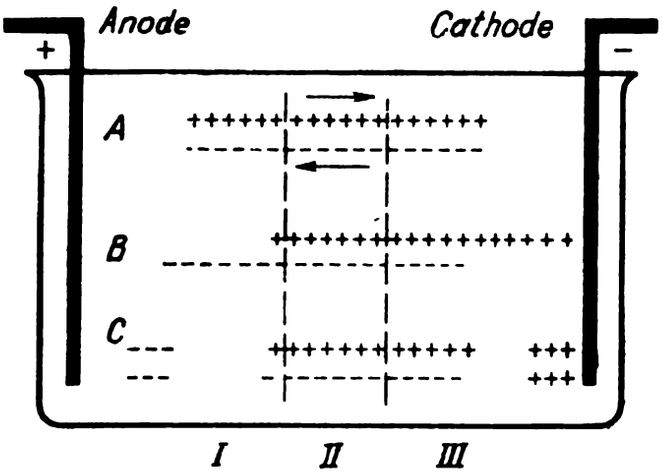



Fig. 17.7. Transference of electricity by ions (determination of transport numbers by the Hittorf method)

The equation derived above makes it possible to compute the transport number if we know the corresponding values of the ionic mobilities. On the other hand, the experimental determination of the transport number allows us to compute the mobilities. It follows from Eqs. (17.22) that

$$U = t_+ (U+V) = t_+ \Lambda$$
$$V = t_- (U+V) = t_- \Lambda$$

i.e. the transport number is not a characteristic of only a given ion, since it depends on the mobility of the ion paired with it. For example, the transport number of a chloride ion in selected electrolytes is expressed by the following quantities:

| Electrolyte | KCl | NaCl | LiCl | HCl |
|---|---|---|---|---|
| $t_-(Cl^-)$ | 0.506 | 0.604 | 0.670 | 0.170 |

The transport numbers are determined experimentally according to the change in the concentrations of the ions at the electrodes (the Hittorf method).

Figure 17.7 shows schematically the motion of the ions (the transference of electricity) in a solution of hydrochloric acid in electrolysis. Let us mentally divide the cell with the electrolyte into three compartments, namely, *I*—the anode compartment (containing the anolyte), *II*—the central part, and *III*—the cathode compartment (containing the catholyte). In electrolysis, the concentration

of the electrolyte in compartment *II* does not change, while it does change in compartments *I* and *III*. The upper part *A* of the drawing schematically shows the distribution of the solute ions. Before electrolysis, the concentration of the solution in all the compartments is the same. Each compartment contains six pairs of ions. The absolute velocity of $H^+$ is approximately five times greater than that of $Cl^-$. For this reason in electrolysis the ions $H^+$ will migrate from left to right during a definite time over a distance that is five times greater than that covered by the ions $Cl^-$ from right to left. As a result five times more ions $H^+$ will migrate to the right through sections *I/II* and *II/III* than ions $Cl^-$ to the left (*B*). Six surplus ions of hydrogen appear in the cathode compartment and there must be the same number of surplus ions of chlorine in the anode compartment. These ions discharge at the electrodes and leave the solution in the form of gases (*C*). One pair of ions remains in the anode compartment and five pairs in the cathode one. The decrease in the amount of electrolyte at the anode $P_A$ (five pairs of ions) is five times greater than that at the cathode $P_C$ (one pair of ions). The ratio $P_A/P_C$ is equal to the ratio of the absolute velocities of a cation and an anion (in our case five). This ratio is equal to the ratio of the mobilities $U/V$.

The transport numbers $t_+$ and $t_-$ can obviously be found from the ratios

$$t_+ = \frac{U}{U+V} = \frac{P_A}{P_A+P_C}; \quad t_- = \frac{V}{U+V} = \frac{P_C}{P_A+P_C} \qquad (17.23)$$

In the example considered above we have $t_+ (H^+) \approx \frac{5}{6} = 0.83$ and $t_- (Cl^-) \approx \frac{1}{6} = 0.17$. Hence it can be seen that the number of ions of a given species participating in the transference of electricity through any cross section of an electrolyte even in the simplest case is in no way related to the number of ions giving up their charge to an electrode. If in electrolysis a substance dissolves at one of the electrodes, Eqs. (17.23) change, but it is still possible to calculate the transport numbers according to the change in the concentration at the electrodes.

Let us consider the electrolysis of a solution of $AgNO_3$ into which silver electrodes are placed. Let the transport numbers of $Ag^+$ and $NO_3^-$ be $t_+$ and $t_-$. Let us pass one faraday of electricity through the solution. The following changes in the numbers of ions will take place at the electrodes. At the anode $t_-$ g-eq of anions will appear and $t_+$ g-eq of cations will disappear. When the current flows, 1 g-eq of cations will pass into the solution from the anode. Thus, in the anode compartment $t_-$ g-eq of anions and $1 - t_+ = t_-$ g-eq of cations will appear, i.e. $t_-$ g-eq of dissolved salt will appear.

At the cathode $t_+$ g-eq of cations will appear, at the cathode 1 g-eq of cations will be liberated, and $t_-$ g-eq of anions will disappear. In the cathode compartment $1 - t_+ = t_-$ g-eq of cations and $t_-$ g-eq of anions will disappear, i.e. $t_-$ g-eq of dissolved salt will disappear. In this case the growth in the amount of salt in the anode compartment will be equal to the decrease in the amount of salt in the cathode compartment, both quantities being equal to the transport number of an anion.

The transport numbers determined according to the Hittorf method are not true ones, since this method does not take solvation of the ions into account. The transport numbers determined according to the Hittorf method are called *apparent transport numbers.*

The concentrations measured in the Hittorf method and the changes in the amount of a substance in the cathode and anode compartments calculated from them are actually determined not only by the quantity of cations and anions entering these compartments and leaving them, but also, as was seen in the cases considered above, by the quantity of solvent transferred by these ions in the form of solvation shells. The shells of ions of different signs are different in size. Let the mean numbers of molecules of water in the solvation shells of the ions $H^+$ and $Cl^-$ be respectively equal to $n$ and $m$. Then in the electrolysis of an HCl solution considered above, the passage of one faraday of electricity will result in the mass of the solvent growing by $\tau_+ n - \tau_- m$ moles in the cathode compartment and in its diminishing by the same value in the anode compartment. Here $\tau_+$ and $\tau_-$ are the *true transport numbers.* The effect considered above can easily be verified by adding to an electrolyte a substance that does not dissociate into ions, for example sugar or urea. After electrolysis the concentration of the added non-electrolyte (calculated with respect to the water) will have changed differently at the electrodes. At one of them it will grow and at the other decrease. Taking into account the changes in the concentration of the added non-electrolyte in determining the transport numbers, we can introduce a correction for the transfer of water from the anode compartment to the cathode one in the form of solvation shells and find the true transport numbers $\tau_+$ and $\tau_-$.

Assume that in the initial electrolyte $N_1$ moles of water contained $N_2$ moles of salt. The transfer of one faraday results in a number of moles of water equal to $\tau_+ n - \tau_- m = y$ migrating from the anode compartment to the cathode one. This reduces the concentration of the dissolved salt. Considering $y$ to be a small quantity in comparison with the number of moles of water in the cathode compartment, we see that the growth in the mass of the water in the cathode compartment leads to an apparent reduction in the number of gramme-ions of salt in the cathode compartment by the quantity $\frac{x_2}{x_1} y$, where

$x_2$ and $x_1$ are the mole fractions of the dissolved salt and water in the solution. To find the true transport number $\tau_+$, this quantity should be added to the quantity $t_+$, namely,

$$\tau_+ = t_+ + \frac{x_2}{x_1} y$$

Obviously

$$\tau_- = t_- - \frac{x_2}{x_1} y$$

Table 17.8 gives the values of $t_+$ and $\tau_+$ for selected electrolytes.

TABLE 17.8

**True $\tau_+$ and Apparent $t_+$ Transport Numbers of Cations of Selected Electrolytes at 25 °C**

($c = 1.3$ g-eq/dm$^3$)

| Salt | $y$ | $t_+$ | $\tau_+$ |
|---|---|---|---|
| HCl | 0.24 | 0.820 | 0.844 |
| LiCl | 1.5 | 0.278 | 0.304 |
| NaCl | 0.76 | 0.366 | 0.383 |
| KCl | 0.60 | 0.482 | 0.495 |
| CsCl | 0.33 | 0.485 | 0.491 |

It should be noted that it is very difficult to accurately determine the quantity $y$, and usually no corrections are introduced into the values of $t_+$ found experimentally according to the Hittorf method. In dilute solutions the difference between $\tau$ and $t$ is less than in concentrated ones, since the ratio $x_2/x_1$ is small.

The dependence of the transport numbers on the concentration is usually not great, it is illustrated by Table 17.9. Sometimes, however, the transport number changes greatly with the concentration and may be equal to zero and even less than zero (for example, for a concentrated solution of $CdI_2$ we have $t_+ < 0$). This can be explained by the formation of complex anions, for example $CdI_4^{2-}$. A growth in the concentration of the solution is accompanied by a growth in the concentration of the complex ions, and for $Cd^{2+}$ the transport number calculated for the entire quantity of cadmium taken as $Cd^{2+}$ without account of complex formation becomes less than zero.

The influence of temperature on the transport number is insignificant. Quite frequently the transport numbers approach 0.5 when the temperature is elevated, i.e. the mobilities of a cation and anion become almost the same. This is not always true, however. For example, the transport numbers in solutions of KCl become less than 0.5 with an increase in temperature (see Table 17.10).

TABLE 17.9

**Dependence of Transport Numbers of Cations $t_+$ on Concentration of Selected Electrolytes in Aqueous Solutions at 25 °C**

| Concentration, g-eq/dm³ | $t_+$ in solutions of | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | HCl | LiCl | NaCl | KCl | $KNO_3$ | $AgNO_3$ | $BaCl_2$ | $K_2SO_4$ | $LaCl_3$ |
| 0.01 | 0.8251 | 0.3289 | 0.3918 | 0.4902 | 0.5084 | 0.4648 | 0.440 | 0.4829 | 0.4625 |
| 0.02 | 0.8263 | 0.3261 | 0.3902 | 0.4901 | 0.5087 | 0.4652 | 0.4375 | 0.4848 | 0.4576 |
| 0.05 | 0.8292 | 0.3211 | 0.3876 | 0.4899 | 0.5093 | 0.4664 | 0.4317 | 0.4870 | 0.4482 |
| 0.1 | 0.8314 | 0.3168 | 0.3854 | 0.4898 | 0.5103 | 0.4682 | 0.4253 | 0.4890 | 0.4375 |
| 0.2 | 0.8337 | 0.3112 | 0.3821 | 0.4894 | 0.5120 | — | 0.4162 | 0.4910 | 0.4233 |
| 0.5 | — | 0.300 | — | 0.4888 | — | — | 0.3986 | 0.4909 | 0.3958 |
| 1.0 | — | 0.287 | — | 0.4882 | — | — | 0.3792 | — | — |

TABLE 17.10

**Transport Numbers $t_+$ at Different Temperatures**

| Temperature, °C | $t_+$ at $c = 0.01$ g-eq in solutions of | | Temperature, °C | $t_+$ at $c \to 0$ in solutions of | |
|---|---|---|---|---|---|
| | HCl | $BaCl_2$ | | KCl | NaCl |
| 0 | 0.846 | 0.387 | 15 | 0.4928 | 0.3929 |
| 18 | 0.833 | 0.397 | 25 | 0.4905 | 0.3962 |
| 30 | 0.822 | 0.404 | 35 | 0.4889 | 0.4002 |
| 50 | 0.801 | — | 45 | 0.4872 | 0.4039 |

Solutions of the same salt in different solvents have different transport numbers. Thus, for $Na^+$ in solutions of NaCl we have:

| Solvent | $H_2O$ | $C_2H_5OH$ | $CH_3COCH_3$ |
|---|---|---|---|
| $t_+$ | 0.402 | 0.471 | 0.397 |

This change in the transport number is mainly explained by the different degree of solvation of the cations and anions depending on the solvent.

**17.11*. Flow of Electric Current through Molten Salts.** The structure of molten salts and oxides is in many ways similar to the crystal ionic lattices which they are formed from in melting. The quasi-crystalline order of alternation of ions having different signs is retained in melts. This order is only insignificantly violated by thermal motion of the ions. It is obvious that at temperatures close to the melting point, a melt contains in a relatively free state the same ions that are characteristic of a salt in the crystalline state. For example, a melt of cryolite contains the ions $AlF_6^{3-}$ and $Na^+$; $Al_2O_3$ dissolved in liquid cryolite produces the ions $Al^{3+}$ and $O^{2-}$. Other ions, for example $AlF_5^{2-}$, $AlF_4^-$, $AlF_2^+$, $AlO^+$, $AlO_3^{3-}$, may form when the temperature is increased, however.

Molten salts have ionic conductivity, and hence Faraday's law can be applied to them. The distances between ions in melts are small, and for this reason the electrostatic interactions of the ions are very great. On the other hand, ions in melts have a great kinetic energy, and it is therefore difficult to speak of the degree of dissociation of melts. Complete dissociation of salts in a melt may be assumed. At comparatively low temperatures, however, the dense packing of the ions prevents their more or less free motion. Every ion in a melt occupies (on an average in time) a site corresponding to the minimum potential energy relative to the neighbouring ions. The position of the ions is similar to that in a crystal lattice in equilibrium. Due to the migration of energy, every ion vibrates about the position of equilibrium. Its potential energy increases when it deviates from this position. Such a displacement of the ions results in violation of the structure of the melt similar to the defects of crystal lattices. Like the defects of the lattice of a semiconductor, the violations in the structure of a melt result first of all in its having electrical conductance. The violations in a melt are incomparably more numerous than in a crystal. Therefore the electrical conductance of molten salts is high and grows with temperature. It was proposed (B. Markov and Yu. Delimarsky) to consider that the fraction of "free" ions not occupying an equilibrium position is the degree of dissociation of a melt and appraise this quantity on the basis of the electrical conductivity. Table 17.11 gives

TABLE 17.11

**Electrical Conductivities of Molten Salts at Temperatures Slightly Exceeding the Melting Points**

| Salt | Temperature, °C | Conductivity, $\Omega^{-1}\cdot cm^{-1}$ | Salt | Temperature, °C | Conductivity, $\Omega^{-1}\cdot cm^{-1}$ |
|---|---|---|---|---|---|
| LiCl | 620 | 5.860 | $MoCl_5$ | 216 | $1.8\times10^{-6}$ |
| NaCl | 805 | 3.540 | $WCl_5$ | 255 | $0.67\times10^{-6}$ |
| KCl | 800 | 2.420 | $UCl_4$ | 570 | 0.340 |
| RbCl | 783 | 1.490 | CuCl | 480 | 3.270 |
| CsCl | 660 | 1.140 | AgCl | 500 | 3.910 |
| LiF | 905 | 20.300 | AgBr | 450 | 2.930 |
| NaF | 1000 | 4.010 | AgI | 600 | 2.520 |
| KF | 860 | 4.140 | $ZnCl_2$ | 336 | 0.0024 |
| NaBr | 800 | 3.060 | $CdCl_2$ | 580 | 1.878 |
| NaI | 700 | 2.560 | $CdBr_2$ | 576 | 1.074 |
| KI | 700 | 1.390 | $CdI_2$ | 399 | 0.209 |
| $AlCl_3$ | 200 | $0.56\times10^{-6}$ | HgCl | 529 | 1.000 |
| $AlBr_3$ | 195 | $0.09\times10^{-6}$ | NaOH | 350 | 2.380 |
| $AlI_3$ | 209 | $2.6\times10^{-6}$ | KOH | 400 | 2.520 |
| $NaNO_3$ | 310 | 0.997 | $Na_2CO_3$ | 850 | 2.370 |
| $KNO_3$ | 350 | 0.666 | $K_2CO_3$ | 950 | 2.120 |
| $InCl_3$ | 594 | 0.417 | $Na_2SO_4$ | 900 | 2.230 |
| $InBr_3$ | 445 | 0.167 | $K_2SO_4$ | 1100 | 1.840 |
| TlCl | 450 | 1.700 | $RbNO_3$ | 341 | 0.490 |
| TlBr | 460 | 0.807 | $CsNO_3$ | 446 | 0.594 |
| $SnCl_2$ | 253 | 0.780 | $LiNO_3$ | 265 | 0.867 |
| $PbCl_2$ | 508 | 1.478 | $AgNO_3$ | 247 | 0.817 |
| $ThCl_4$ | 814 | 0.640 | $CaCl_2$ | 800 | 2.020 |
| $BiCl_3$ | 250 | 0.406 | $MgCl_2$ | 800 | 1.700 |
| $TeCl_4$ | 236 | 0.115 | $Na_3AlF_6$ | 1020 | 2.670 |

the values of the electrical conductivities of selected molten salts at temperatures close to the melting points. These values exceed the conductivities of aqueous electrolytes of moderate concentrations scores of times. If we take into consideration the high concentration of molten salts and their high temperature, the conductivity of melts should be acknowledged as being comparatively low. Indeed, the equivalent conductivities of potassium halides at 750-900 °C are about 90-120 $cm^2/g\text{-}eq\cdot\Omega$, and for the chlorides of calcium, strontium and barium at the melting points it varies from 50 to 60 $cm^2/g\text{-}eq\cdot\Omega$.

The conductivity of molten salts, as a rule, grows with the temperature (exceptions are the salts of mercury, indium and certain others). The conductivity grows especially rapidly at temperatures slightly exceeding the melting points.

The electrostatic theory of solutions explains the comparatively low conductivity of molten salts by the enormous retarding effect of the ionic atmosphere, which also consists of ions of the opposite sign closely surrounding every ion. There is no solvent reducing the interaction of the ions, and the distances between ions are very small. Owing to the absence of solvation, the mobilities of ions in

melts are directly related to their radii. In the series of alkali metal cations a regular sequence of mobilities is observed, namely, $U_{Li^+} > U_{Na^+} > U_{K^+}$.

The structure of molten salts differs appreciably from that of electrolytic solutions, and the laws characteristic of solutions should not be mechanically transferred to melts, and vice versa.

The dependence of the conductivity on the composition for mixtures of molten salts varies quite considerably, and this dependence is sometimes very complicated. Figure 17.8 shows curves of the dependence of the molar conductivity of the binary system $CaCl_2$-KCl on the composition. These curves have a minimum. Curves showing the dependence of the conductivity on the composition for some melts, for example KCl-$ZnSO_4$ and the melt $K_2SO_4$-$ZnSO_4$ have a complicated configuration (Fig. 17.9), which points to the formation of complex ions. The result is that the ionic composition of the melt sharply changes with a change in the concentration. The relative temperature coefficient of conductivity $K$ is also shown in Fig. 17.9.

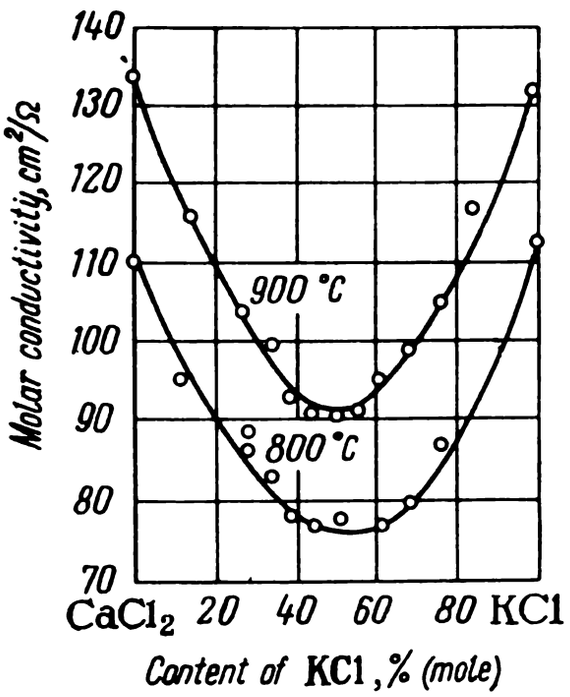



Fig. 17.8. Molar conductivity of binary melt $CaCl_2$-KCl

Cases are known when melts of two substances have a good conductance, although separate melts of each of them do not conduct current. An example is the melt $AlBr_3$-$SbBr_3$. Here complexes are apparently formed that decompose into ions (see Sec. 17.7).

The transport numbers can obviously be determined only for melts of several salts. The results indicate the complicated structure of melts, which influences the participation of separate ions in the transfer of electricity. Thus, in the melt KCl + $MgCl_2$ the value of $t_+(K^+) = 0.70$ and $t_+(Mg^{2+}) = 0.14$, while in the melt 2KCl + $MgCl_2$ we have $t_+(K^+) = 0.72$-$0.79$ and $t_+(Mg^{2+}) = 0.0$.

The investigation of the electrical conductance of binary and more complicated salt melts depending on the composition and temperature is a valuable method of physicochemical analysis which makes it possible to study the interaction of the components in a melt.

**17.12*. Conductance of Solid Salts.** At room temperature solid salts (with a few exceptions, for example $Ag_2HgI_4$) conduct electricity very poorly. With a growth in temperature they frequently become good conductors having some interesting features.

Thus, in the electrolysis of hydrides (LiH, $CaH_2$) hydrogen is liberated not at the cathode, as usual, but at the anode. This circumstance points to the fact that not protons, but negatively charged hydrogen ions ($H^-$) migrate in a hydride and they discharge at the anode.

Very often so-called *unipolar* (unidirectional) conductance appears in solid salts. An electric current in them is the result of the motion of either only positive or only negative ions. The presence of unipolar conductance can be proved experimentally. We can, for example, clamp several pieces of silver iodide between silver electrodes and pass a current through this conductor at an elevated temperature. After passing 96.5 C of electricity through the salt, we take the system apart and weigh its component parts. The mass of the silver anode will be found to decrease by 108 mg, the mass of the cathode will increase by the same amount,

and the mass of the pieces of AgI will remain unchanged. These results indicate that only ions of silver carry a current in crystalline AgI. Thus, for solid AgI we have $t_+ = 1$ and $t_- = 0$.

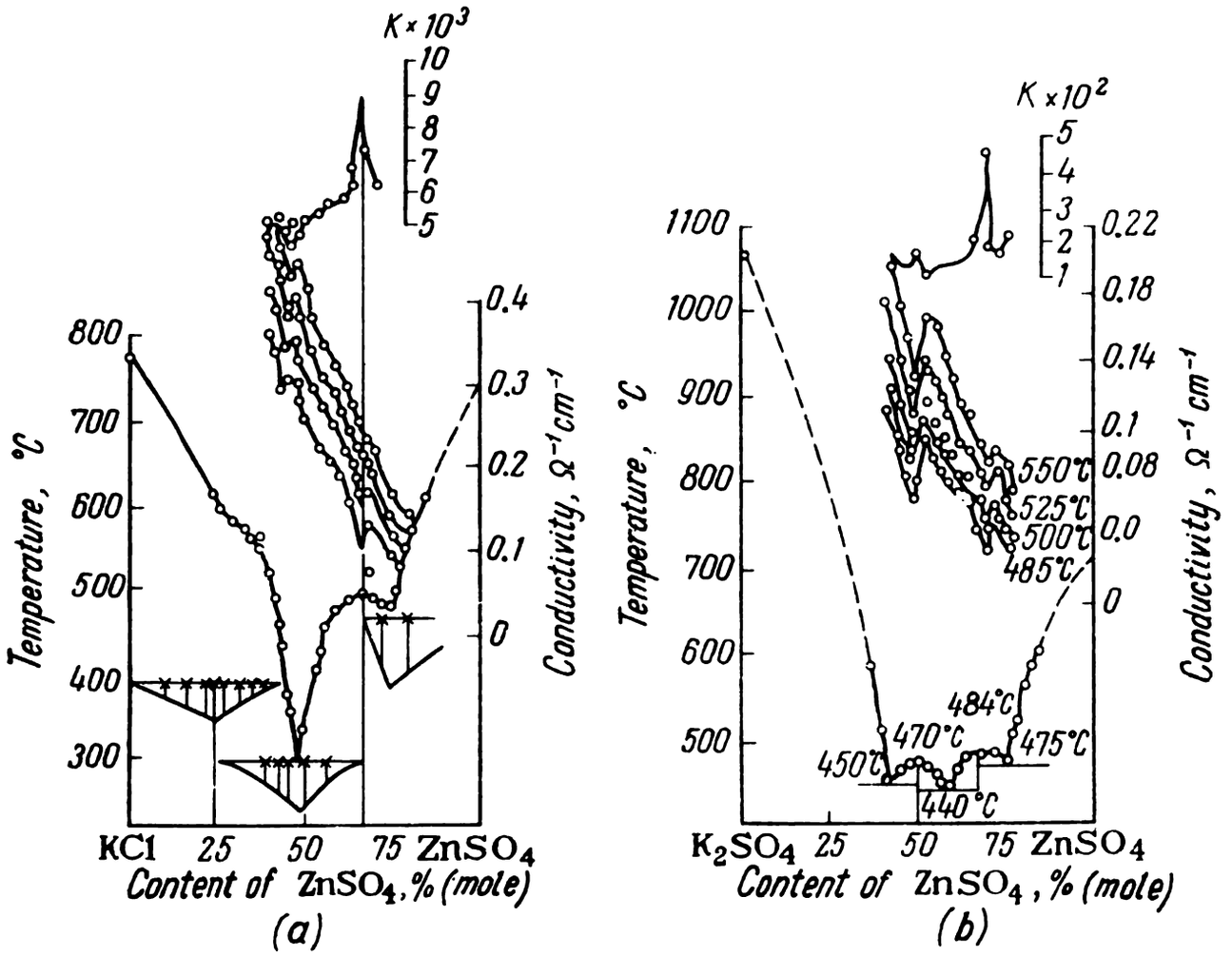



Fig. 17.9. Dependence of conductivity on composition:
*a*—for melt $KCl-ZnSO_4$; *b*—for melt $K_2SO_4-ZnSO_4$; **K**—relative temperature coefficient of conductivity

Current is transferred only by cations ($t_+ = 1$) in the following salts:

| | | | |
|---|---|---|---|
| NaCl, KCl, NaF | . . .below 400-500 °C | AgBr | . . .at 300 °C |
| AgCl | . . .at 350 °C | AgI | . . .at 400 °C |
| | | CuI | . . .at 400-500 °C |
| | | $Cu_2S$ | . . .at 200 °C |

The reverse phenomenon is frequently observed, i.e. only anions have mobility ($t_- = 1$):

| | |
|---|---|
| $BaF_2$ . . . | at 500 °C |
| $BaCl_2$ . . . | at 400-700 °C |
| $BaBr_2$ . . . | at 250-365 °C |
| $PbF_2$ . . . | at 200 °C |
| $PbBr_2$ . . | at 250-365 °C |

The second ion frequently begins to participate in the conduction of electricity when the temperature is elevated, and the transport number of the first ion becomes less than unity. In addition, changes from an ionic to cationic conductance and vice versa are possible. Thus, for $PbI_2$ at 155 °C we have $t_- = 1$, and at 376 °C we have $t_+ = 1$.

Unipolar conductance is mainly explained by the presence in the salt lattice of free (vacant) cation or anion points. These vacant points ("holes") carry an effective charge and migrate in an electric field, creating an electric current.

Crystals of NaCl become conductive at 620 °C, when $t_+ = 0.883$ and $t_- = 0.117$, i.e. electricity is mainly carried by sodium ions. Solid salts are sometimes characterized by electronic conductivity, and also by mixed conductivity, i.e. electricity is carried both by ions and by electrons. Thus, the conductance of $Ag_2S$ (β) is 80% ionic and 20% electronic. A transition from ionic to mixed conductivity is characteristic of CuCl at a high temperature.

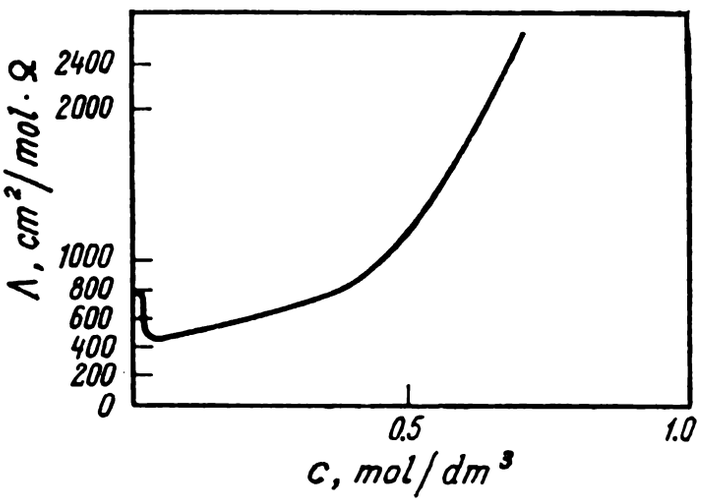



Fig. 17.10. Dependence of equivalent conductivity of sodium solutions in liquid ammonia on concentration

**17.13*. Conductance of Solutions in Liquid Ammonia.** Liquid ammonia is capable of dissolving the alkali metals with the formation of coloured solutions having a good electrical conductance. The latter is due to the interaction between atoms of the alkali metal and ammonia molecules, the result being ionization of the metal atoms; the electrons are bound by ammonia molecules:

$$Me + NH_3 \rightleftharpoons Me^+ + NH_3^-$$

With a growth in the concentration, the equivalent conductivity first decreases, as in aqueous solutions, and then (at concentrations above 0.05 *N*) sharply grows and reaches values characteristic of metals. Thus the curve of conductivity versus concentration for sodium has a sharply expressed minimum (Fig. 17.10). This is explained by the fact that with relatively low concentrations of the sodium in a solution, the electrons detached from the sodium atoms are completely bound by molecules of the ammonia. As a result the negative ions $NH_3^-$ unusual for ammonia are formed, i.e. the conductance becomes ionic and, therefore, decreases with the concentration. Apparently at concentrations above 0.05 *N* the electrons detached by the sodium atoms are no longer completely bound by ammonia molecules and, remaining free, result in a very high electronic conductance.

**17.14*. Methods of Measuring Electrolyte Conductivity.** To accurately measure the conductivity of an electrolyte, it is necessary to (1) accurately measure the temperature and keep it constant with the aid of a thermostat; (2) eliminate polarization of the electrodes (i.e. a change in the state of their surface and in the concentration of the electrolyte around them in the process of measurements), and (3) accurately measure electrical quantities.

Polarization can be eliminated by platinizing platinum electrodes (i.e. coating them by electrolysis with a fine layer of platinum black and thus increasing the surface area of the electrodes) and by using alternating current with a frequency of 500 to 2000 Hz to eliminate concentration polarization. Cells of the most diverse shapes are used to measure conductivity. The cell is provided with two identical flat parallel electrodes so secured that the distance between them will not change. Figure 17.11 shows shapes of cells recommended for the determination of the conductivity at high and low concentrations. A device for measuring the conductance is shown schematically in Fig. 17.12. It consists of circuit *abc*. The cell for measuring the conductance is connected to the circuit

between $b$ and $c$. Its resistance is denoted by $R_c$. A resistance box $R$ is connected between $a$ and $c$. Section $ab$ is a thin metal (Pt, Mn, manganine, etc.) homogeneous wire one metre long stretched over a graduated rule. Conductors feeding an alternating current from the secondary winding of a Ruhmkorff coil $v$ or from an

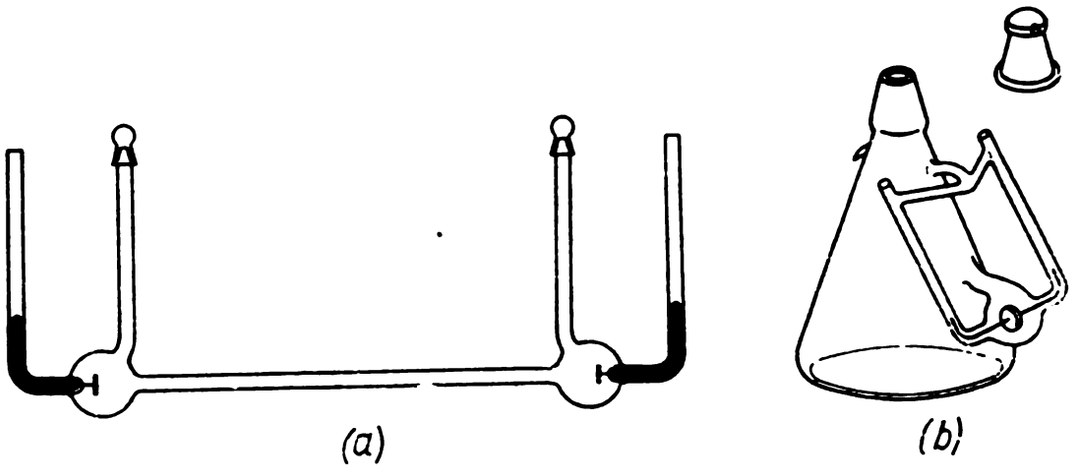



Fig. 17.11. Cells for measuring conductivity:
$a$—at high concentrations; $b$—at low concentrations

audio-frequency generator are connected to points $a$ and $b$. To prevent electrolysis and polarization, an alternating current, and not a direct one, is used for determining the resistance of a liquid. A low-ohmic telephone or a cathode oscillograph is a very sensitive instrument for detecting current when an alternating current is used. This instrument ($T$) is connected between point $c$ and movable contact $d$.

The resistance of the solution is determined at such a position of contact $d$ when no sound is heard in the telephone receiver and, consequently, there is no current in line $cd$. With this position of the contact, according to Kirchhoff's law, the resistances $R$, $R_c$, $r_1$ and $r_2$ are related by the equation

$$\frac{R}{R_c}=\frac{r_1}{r_2}$$

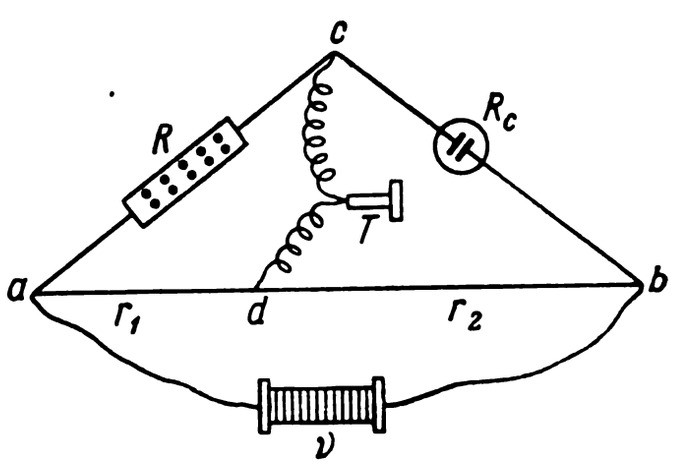



Fig. 17.12. Device for measuring conductance of electrolyte

Since the wire is homogeneous, the resistances $r_1$ and $r_2$ of sections $ad$ and $db$ are proportional to their lengths, i.e.

$$\frac{R}{R_c}=\frac{ad}{db} \quad \text{or} \quad R_c=R\frac{db}{ad}$$

The total resistance of the cell with the solution and the resistivity $\rho$ of the solution are related by the equation

$$R_c=\rho\frac{l}{A} \quad \text{or} \quad R_c=\rho K_c$$

where $K_c = l/A$ is called the *cell constant*
$l$ = distance between electrodes
$A$ = area of each electrode.

The electrical conductivity $\varkappa = 1/\rho$, and therefore

$$\varkappa = \frac{K_c}{R_c}$$

The cell constant $K_c$ is found according to the same formula. For this purpose the resistance $R_c$ of a solution of potassium chloride having a known conductivity and poured into a cell is measured.

TABLE 17.12

**Conductivity of Solutions of Potassium Chloride**

| Molality of solution (approximate) | Exact composition of solution in g KCl per kg of solution [1] | $\varkappa$, $\Omega^{-1}$ cm$^{-1}$ | | |
|---|---|---|---|---|
| | | 0 °C | 18 °C | 25 °C |
| 1 | 74.1352 | $0.06517_6$ | $0.09783_8$ | $0.11134_2$ |
| 0.1 | 7.41913 | $0.007137_9$ | $0.011166_7$ | $0.012856_0$ |
| 0.01 | 0.745263 | $0.0007736_4$ | $0.0012205_2$ | $0.0014087_7$ |

[1] Reduced to conditions in a vacuum.

The conductivities of standard solutions of KCl according to the data of G. Jones and B. Bradshaw are given in Table 17.12. The mass concentrations of the solutions indicated in the table do not depend on possible changes in molecular masses and the standard unit of volume in the future.

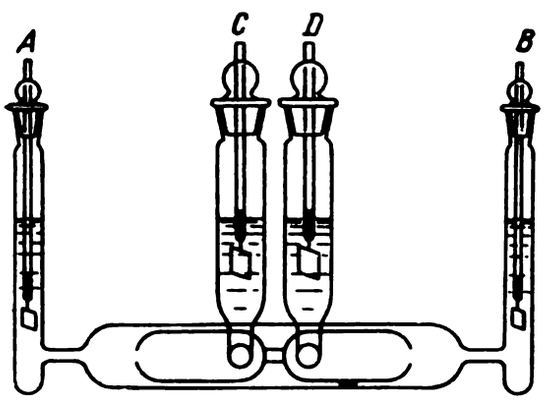



Fig. 17.13. Device for measuring conductance of electrolyte with the use of a direct current

The use of an alternating current makes it possible to measure the conductivity of electrolytes with a high accuracy. Here difficulties arise, however, that are due to the presence of electric capacitance and self-induction (especially the former) in the circuit, while it is necessary to measure only the resistance. When a direct current is used these difficulties vanish, but concentration polarization appears. To prevent this, the potential difference is measured between special strictly reversible electrodes that are at a considerable distance from the feeding electrodes. Modern potentiometry allows $U$ to be measured with an accuracy up to 0.0001%. Figure 17.13 shows a cell for use with a direct current, where $C$ and $D$ are electrodes for measuring the potential difference, and $A$ and $B$ are the feeding electrodes. The potential difference $U_1$ with a current of constant intensity flowing between electrodes $A$ and $B$ and the potential difference $U_0$ across the ends of an accurately known resistance $R_0$ connected in series with the cell are measured. The resistance being sought $R_1$ is determined from the equation

$$\frac{U_1}{R_1} = \frac{U_0}{R_0} \tag{17.24}$$

**17.15*. Methods of Measuring Transport Numbers.** Three experimental methods are used for determining transport numbers, namely, (1) the classical Hittorf method, (2) the moving boundary method, and (3) a method connected with the determination of the diffusion potential.

The *Hittorf method*, employed by its author during several decades beginning from 1853, is still being used without any alterations of principle (only certain technical improvements have been introduced). A cell for determining the transport numbers by the Hittorf method consists of an anode, a cathode and an intermediate compartments. The electrolyte in each of the compartments can be investigated separately.

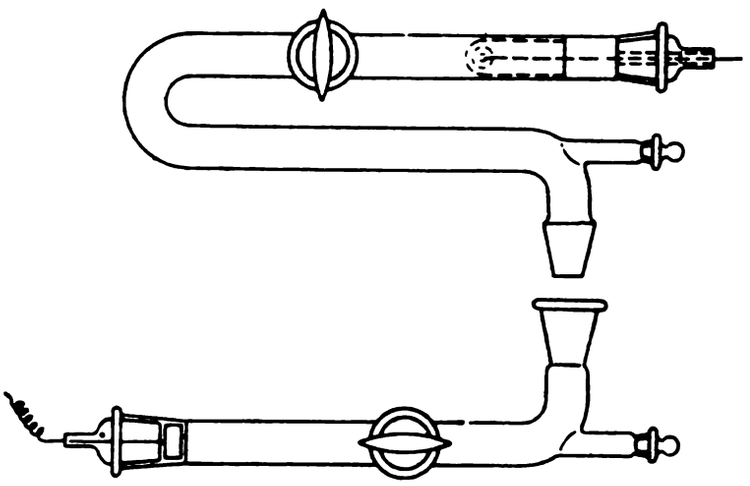


Fig. 17.14. Washburn's cell for determining the transport numbers according to the Hittorf method

Figure 17.14 shows a cell for the determination of transport numbers proposed by H. Washburn. The anode compartment (at the left) contains an anode in the form of a silver coil coated with crystals of silver, and the cathode compartment a silver disk coated with granulated AgCl. The Washburn cell can also be used for determining the change in the concentration of an undissociating component in measuring true transport numbers.

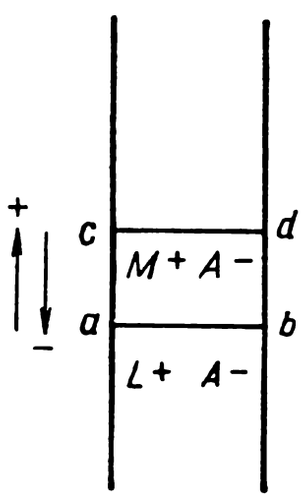



Fig. 17.15. Diagram showing how the transport numbers are determined by the moving boundary method

The *moving boundary method* consists in watching the movement of boundary *ab* between two solutions of different density when a current flows through them (Fig. 17.15). The solutions have a common ion, for example anion $A^-$. The indicator solution containing $L^+A^-$ with the greater density is beneath the solution containing $M^+A^-$ and having the concentration *c*. The current flows in such a direction that the cations migrate upward. It is essential that the mobility of the ion $L^+$ be greater than that of the ion $M^+$. In a definite time after the beginning of the flow of current (assume that *q* coulombs of electricity have passed through the solutions), the boundary moves from *ab* to *cd*. It is obvious that during this time cross section *cd* was passed upward by cations $M^+$ in the volume *abcd* equal to $V$ cm$^3$, i.e. $cV$ g-eq $M^+$. Hence the transport number of the cation $M^+$ is

$$t_+ = \frac{VcF}{q} \tag{17.25}$$

Account must be taken of the change in the volume of the solution as a result of electrochemical reactions. The initial boundary *ab* between the two electrolytes can be fixed on a porous glass partition, and then the amount of the cation $L^+$ passing upward through the partition during the flow of current can be found analytically. In this case the transport number is determined for the cation $L^+$, and the cation $M^+$ becomes the indicator.

# CHAPTER 18

# EQUILIBRIA IN IONIC SOLUTIONS

**18.1. General.** The dissociation of solutes into ions obeys the same laws of chemical equilibrium as other reactions. The presence of charges in the ions formed naturally has no bearing on the applicability of the first and second laws of thermodynamics and all the conclusions following from them.

When considering ionic equilibria in real solutions, we must decide every time whether we can use an equation of equilibrium in the given specific case that holds for ideal solutions, or whether the concentrations in this equation should be replaced by the activities.

Weak electrolytes dissociate into ions only insignificantly. For this reason the ionic strength of such solutions is not great even with comparatively great concentrations. We therefore make only a small error in calculating equilibrium if we use the values of the concentrations of ions and molecules instead of the activities.

If a solution is a mixture of electrolytes, the ionic strength of the solution depending on the total concentration of ions may be so great that in calculating equilibrium it is necessary to change over from analytical concentrations to activities even for ions whose concentration is low. It is sometimes sufficient to introduce only the activities of the ions into the expression for the equilibrium constant, since the activity of the undissociated molecules depends very slightly on the ionic strength.

The concentration of ions (g-ion/dm$^3$) is found by multiplying the concentration of the electrolyte (mol/dm$^3$) by the degree of dissociation $\alpha$ and by the factor $z$ showing how many ions of a given species are formed upon the decomposition of one molecule. For example, in the electrolytic dissociation of $AlCl_3$ for $Al^{3+}$ we have $z = 1$, and for $Cl^-$ we have $z = 3$. If the molarity $c$ of a solution is equal to 0.1 and $\alpha = 0.4$, the concentration of the $Al^{3+}$ ions will be $0.1 \times 1 \times 0.4 = 0.04$ g-ion/dm$^3$, and that of the $Cl^-$ ions will be $0.1 \times 3 \times 0.4 = 0.12$ g-ion/dm$^3$.

The dissociation of strong electrolytes is equal to 100% (or almost 100%), so that the concentrations of the ions may be assumed equal to the molarity of the substance being considered multiplied by the corresponding value of $z$. Owing to the complete dissociation of

strong electrolytes, the ionic strength of their solutions rapidly grows with an increase in the concentration. For this reason the activity of ions may be considered equal to their concentration only in infinitely dilute solutions.

Strong, even completely dissociated electrolytes with sufficiently great concentrations form ionic pairs, so that not all the ions, but only part of them are actually free. Solutions of strong electrolytes also sometimes contain real undissociated particles, for example $PbCl^+$ or TlCl. The presence of both ionic pairs and undissociated particles allows us to speak of ionic equilibrium in strong electrolytes.

**18.2. Dilution Law.** In the dissociation of a weak electrolyte equilibrium sets in between undissociated molecules and ions. Let us consider the simplest example when a molecule decomposes only into two ions, namely,

$$CH_3COOH + H_2O = CH_3COO^- + H_3O^+ \tag{18.1}$$

On the basis of the law of mass action we have

$$K_a = \frac{a_{CH_3COO^-} a_{H_3O^+}}{a_{CH_3COOH} a_{H_2O}} \tag{18.2}$$

Like any equilibrium constant, $K_a$ depends on the temperature. In dilute solutions the activity of the solvent (in the present case water) can be considered constant. This allows us to transfer $a_{H_2O}$ to the left-hand part of Eq. (18.2). Let us denote the product $K_a \cdot a_{H_2O}$ by $K_{d,\,CH_3COOH}$. Hence

$$K_{d,\,CH_3COOH} = \frac{a_{CH_3COO^-} a_{H_3O^+}}{a_{CH_3COOH}} \tag{18.3}$$

The quantity $K_d$ is called the *thermodynamic dissociation constant* or simply the *dissociation constant.*

Water is also an electrolyte, but not a strong one, since it weakly dissociates into ions. It simultaneously serves as a solvent. In this connection the reaction of dissociation proceeds according to the equation

$$H_2O + H_2O = H_3O^+ + OH^-$$

On the basis of the law of mass action we have

$$K_a = \frac{a_{OH^-} a_{H_3O^+}}{a_{H_2O} a_{H_2O}} \tag{18.4}$$

Since the concentration of the ions $OH^-$ and $H_3O^+$ formed is very low, we can consider that the activity of the undissociated molecules of water does not depend on the degree of dissociation. Let us transfer $a_{H_2O}$ to the left-hand part of Eq. (18.4) and denote the product

$K_a \cdot a_{H_2O}$ by $K_{d,\,H_2O}$. Hence

$$K_{d,\,H_2O} = \frac{a_{H_3O^+} a_{OH^-}}{a_{H_2O}} \tag{18.5}$$

The quantity $K_{d,\,H_2O}$ is the thermodynamic dissociation constant of water, while the product $K_{d,\,H_2O} \cdot a_{H_2O}$, designated $K_w$, is called the *ionic product of water*:

$$K_w = a_{H_3O^+} a_{OH^-} \tag{18.6}$$

The thermodynamic dissociation constant and the ionic product of water depend on the temperature. The change in the dissociation constant with a growth of the temperature is usually not great. For example for the acids listed in Table 18.1, a growth of the temperature from 0 to 20 °C is accompanied by a change in the dissociation constant by only 3-8%. In the same temperature interval the ionic product of water grows more than six times.

TABLE 18.1

**Influence of Temperature on Dissociation Constants of Acids and on Ionic Product of Water**

| Acid | Dissociation constant ($K_d \times 10^5$) at temperature | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 °C | 10 °C | 20 °C | 30 °C | 40 °C | 50 °C | 60 °C |
| Formic | 16.38 | 17.28 | 17.65 | 17.68 | 17.16 | 16.50 | 15.51 |
| Acetic | 1.657 | 1.729 | 1.753 | 1.750 | 1.703 | 1.633 | 1.542 |
| Propionic | 1.274 | 1.326 | 1.338 | 1.326 | 1.280 | 1.229 | 1.160 |
| *n*-Butyric | 1.578 | 1.579 | 1.551 | 1.489 | 1.395 | 1.302 | 1.199 |
| $K_w \times 10^{-14}$ | 0.13 | 0.36 | 0.86 | 1.89 | 3.80 | 5.60 | 12.6 |

A glance at Table 18.1 shows that the values of the dissociation constants for weak acids dissolved in water pass through a maximum which for the acids given in the table is in the interval between 0 and 60 °C. This can be explained by the influence of two opposite actions. On one hand, any dissociation proceeds with the absorption of heat, and, therefore, with an increase in temperature equilibrium should be displaced in the direction of a greater degree of dissociation. On the other hand, with a growth in temperature the relative permittivity of the water serving as a solvent decreases, and this facilitates recombination of the ions. The dissociation constant reaches its maximum value at the temperature at which the influence of the second factor begins to predominate.

The ionic product of water continuously grows with the temperature. Table 18.1 shows how it changes up to 60 °C. At 100 °C its value is $K_w = 74 \times 10^{-14}$ and at 200 °C we have $K_w = 400 \times 10^{-14}$.

Replacing the activities by the products of the analytical concentrations and the corresponding activity coefficients, we obtain for example using the molality

$$K_{d,\,CH_3COOH} = \frac{m_{CH_3COO^-} m_{H_3O^+}}{m_{CH_3COOH}} \frac{\gamma'_{CH_3COO^-} \gamma'_{H_3O^+}}{\gamma'_{CH_3COOH}} \tag{18.7}$$

Let us introduce the notation

$$\frac{m_{CH_3COO^-} m_{H_3O^+}}{m_{CH_3COOH}} = k_m \tag{18.8}$$

Hence

$$K_{d,\,CH_3COOH} = k_m \frac{\gamma'_{CH_3COO^-} \gamma'_{H_3O^+}}{\gamma'_{CH_3COOH}} \tag{18.9}$$

In the same way we can express the thermodynamic dissociation constant through the molarity $c$ and the corresponding activity coefficients $f$. Introducing the notation

$$\frac{c_{CH_3COO^-} c_{H_3O^+}}{c_{CH_3COOH}} = k_c \tag{18.10}$$

we get

$$K_{d,\,CH_3COOH} = k_c \frac{f_{CH_3COO^-} f_{H_3O^+}}{f_{CH_3COOH}} \tag{18.11}$$

Let us express the total concentration of an electrolyte in mol/dm$^3$ through $c$ (molarity), and denote the degree of dissociation by $\alpha$. Hence[1]

$$[CH_3COO^-] = c\alpha; \quad [H_3O^+] = c\alpha \text{ and } [CH_3COOH] = c\,(1-\alpha)$$

The equation for $k_c$ acquires the form

$$k_c = \frac{\alpha^2 c}{1-\alpha} \tag{18.12}$$

This equation is the simplest form of the *dilution law* formulated by W. Ostwald in 1888. It is obvious that the greater the value of $k_c$, the higher is the degree of dissociation. Thus the quantity $k_c$ can serve as a measure of the strength of an acid, i.e. as a measure of acidity. For moderately weak electrolytes, for example $H_3PO_4$ (first stage), $Ca(OH)_2$ and $CHCl_2COOH$, the values of $k_c$ range from $10^{-2}$ to $10^{-4}$. For weak electrolytes, for example $CH_3COOH$ and $NH_4OH$, the values of $k_c$ range from $10^{-5}$ to $10^{-9}$. When $k_c$ is less

[1] In the following we shall frequently use the notation $[CH_3COOH] = c_{CH_3COOH}$ to express concentrations.

than $10^{-10}$ the electrolyte is considered to be very weak. Such electrolytes include $H_2O$, $C_6H_5OH$, $C_6H_5NH_2$ and HCN.

If the degree of dissociation is very low, the quantity $\alpha$ may be neglected in comparison with unity, and Eq. (18.12) becomes

$$k_c = c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{k_c}{c}} \tag{18.13}$$

i.e. the degree of dissociation is inversely proportional to the square root of the concentration of the electrolyte.

If an electrolyte dissociates into more than two ions, the dependence of $k_c$ on the degree of dissociation correspondingly becomes more complicated. For example, in the dissociation of $CaCl_2$ we have

$$[Ca^{2+}] = c\alpha; \quad [Cl^-] = 2c\alpha \text{ and } [CaCl_2] = c(1-\alpha)$$

whence

$$k_c = \frac{c\alpha(2c\alpha)^2}{c(1-\alpha)} = \frac{4c^2\alpha^3}{1-\alpha} \tag{18.14}$$

Correspondingly at a low degree of dissociation we have

$$\alpha = \sqrt[3]{\frac{k_c}{4c^2}} \tag{18.15}$$

It can be noted that for electrolytes dissociating into two ions the value of $k_c$ is equal to one-fourth of the concentration at which $\alpha = \frac{1}{2}$.

In dilute solutions the values of the mobilities $U$ and $V$ insignificantly differ from their limiting values ($U \approx U_\infty$ and $V \approx V_\infty$). Therefore, dividing Eq. (17.13) by Eq. (17.14) we get

$$\alpha = \frac{\Lambda}{\Lambda_\infty} \tag{18.16}$$

Inserting Eq. (18.16) into Eq. (18.12), we have

$$k_c = c\frac{\Lambda^2}{\Lambda_\infty^2\left(1-\frac{\Lambda}{\Lambda_\infty}\right)} = c\frac{\Lambda^2}{\Lambda_\infty(\Lambda_\infty-\Lambda)} \tag{18.17}$$

The quantity $k_c$ is constant only for very dilute solutions whose activity coefficients can be considered equal to unity. In general $k_c$ is a variable quantity. Some authors call $k_c$ the *classical dissociation constant*, but it is more correct to call it a *classical function of dissociation* or simply a *dissociation function*.

If the ionic strength of a solution is sufficiently low, the activity coefficient for undissociated acetic acid $f_{CH_3COOH}$ is close to unity and Eq. (18.11) becomes

$$K_{d,\,CH_3COOH} = k_c f_{CH_3COO^-} f_{H_3O^+} \tag{18.18}$$

The thermodynamic dissociation constant $K_{d,\,CH_3COOH}$ in Eqs. (18.11) and (18.18) does not depend on the concentration.

**18.3. Thermodynamic Dissociation Constant.** For accurate calculations of ionic equilibria the thermodynamic dissociation constant from Eq. (18.18) should be used. The activity coefficients are calculated by Eqs. (16.48), (16.50) or (16.52) (see Sec. 16.7). In the simplest case, when a molecule dissociates into two ions, on the basis of Eq. (18.9) at $\gamma'_{CH_3COOH} = 1$ we have

$$\log K_{d,\,CH_3COOH} = \log k_m + 2\log \gamma'_{\pm} \qquad (18.19)$$

For dilute solutions [see Sec. 16.7, Eq. (16.48)]

$$\log \gamma'_{\pm} = -Az_1z_2\sqrt{I}; \quad I = \frac{1}{2}\sum m_i z_i^2 \quad \text{and} \quad m_i = m\alpha$$

After inserting these values we obtain

$$\log K_{d,\,CH_3COOH} = \log k_m - 2Az_1z_2\sqrt{\frac{1}{2}(m_1\alpha z_1^2 + m_2\alpha z_2^2)} \qquad (18.20)$$

But in the example with acetic acid considered above $z_1 = z_2 = 1$, therefore

$$\log K_{d,\,CH_3COOH} = \log k_m - 2A\sqrt{m\alpha} \qquad (18.21)$$

In aqueous solutions

$$A = \frac{1.823\times10^6}{(\varepsilon_r T)^{3/2}} = \frac{1.823\times10^6}{(78.25\times298.2)^{3/2}} = 0.512 \text{ (at 25 °C)}$$

[see Sec. 16.7, Eq. (16.48)]

$$\log K_{d,\,CH_3COOH} = \log k_m - 1.024\sqrt{m\alpha} \qquad (18.22)$$

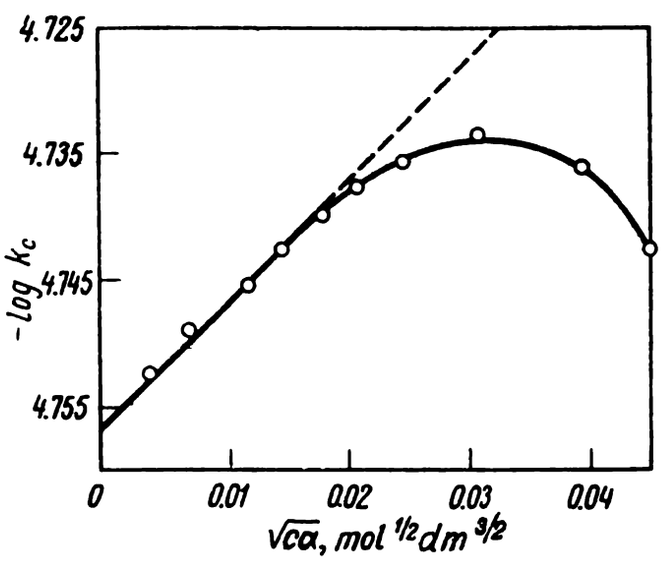



Fig. 18.1. Dependence of $-\log k_c$ on $\sqrt{c\alpha}$ for aqueous solution of $CH_3COOH$

This is an equation of a straight line in the coordinates $\log k_m$ versus $\sqrt{m\alpha}$. For dilute solutions the values of $m$ (molality) and $c$ (molarity) are very close, the same as the values of the corresponding activity coefficients $\gamma'$ and $f$. Substituting $c$ for $m$ and $f$ for $\gamma'$, we get a similar equation in the coordinates $\log k_c$ versus $\sqrt{c\alpha}$ (Fig. 18.1). A glance at the figure shows that there is a linear relation between $\log k_c$ and $\sqrt{c\alpha}$ at low values of the latter.

With a growth in concentration the dissociation function $k_c$ gradually grows and then passes through a maximum. The experimental data used to plot the diagram in Fig. 18.1 are given in Table 18.2. The first line of this table has been found by extrapolation.

TABLE 18.2

**Main Parameters of Process of Dissociation of Acetic Acid in Aqueous Solution at 25 °C**

| c | Λ | α | $k_c \times 10^5$ | $K_d \times 10^5$ |
|---|---|---|---|---|
| 0 | 390.59 | 1.000 0 | 1.752 | 1.752 |
| 0.000 028 01 | 210.32 | 0.538 4 | 1.768 | 1.752 |
| 0.000 111 35 | 127.71 | 0.327 0 | 1.779 | 1.754 |
| 0.000 218 44 | 98.47 | 0.247 0 | 1.781 | 1.751 |
| 0.001 028 3 | 48.13 | 0.123 2 | 1.797 | 1.750 |
| 0.002 414 0 | 32.21 | 0.082 45 | 1.809 | 1.750 |
| 0.009 842 1 | 16.367 | 0.041 90 | 1.832 | 1.746 |
| 0.020 000 | 11.567 | 0.029 60 | 1.840 | 1.738 |
| 0.050 000 | 7.356 | 0.018 83 | 1.854 | 1.723 |
| 0.100 00 | 5.200 | 0.013 31 | 1.846 | 1.695 |
| 0.200 00 | 3.650 | 0.009 345 | 1.821 | 1.645 |

The thermodynamic dissociation constant $K_{d,\,CH_3COOH}$ calculated by Eq. (18.20) remains practically constant to a concentration of 0.01 mol/dm³. Then it begins to drop.

**18.4. Determination of True Degree of Dissociation.** Equation (18.16) for calculating the degree of dissociation of electrolytic solutions compares the equivalent conductivity at a given dilution corresponding to a certain finite average distance between the ions present and the equivalent conductivity at infinite dilution, i.e. in conditions when the distances between the ions are infinitely great. The mobility of ions depends on the distances between them. For this reason it is more correct to compare the equivalent conductivity Λ at the given dilution with the equivalent conductivity Λ′ of a solution, which cannot be obtained in practice, having the same concentration of the ions, but completely dissociated. Thus, the true value of the degree of dissociation can be found from the formula

$$\alpha = \frac{\Lambda}{\Lambda'} \tag{18.23}$$

The equivalent conductivity of such a solution is naturally smaller than $\Lambda_\infty$ of the solution being investigated, for this reason the true degree of dissociation [Eq. (18.23)] is always greater than the degree of dissociation calculated by Eq. (18.16).

The method of calculating the quantity Λ′ replacing $\Lambda_\infty$ was proposed by L. Onsager, who derived a formula for mono-monovalent

electrolytes

$$\Lambda' = \Lambda_\infty - \left[\frac{8.20 \times 10^5}{(\varepsilon_r T)^{3/2}} \Lambda_\infty + \frac{82.4}{(\varepsilon_r T)^{1/2}\,\eta}\right] \sqrt{c'} \qquad (18.24)$$

where $c'$ is the concentration of the ions, g-ion/dm$^3$.

For very dilute solutions of strong electrolytes Eq. (18.24) is well confirmed by experimental data (Fig. 18.2). In complete dissociation of mono-monovalent electrolytes, $c'$ is equal to the molarity $c$. In incomplete dissociation the quantity $c'$ must be replaced by the product $c\alpha$, where $c$ is the molarity of the solution and $\alpha$ the degree of dissociation. It should be noted in addition that $\varepsilon_r$—the relative permittivity of the medium and $\eta$—the viscosity of the medium are constant quantities at a constant temperature in a dilute solution. Introducing the values of these quantities at 298 K into Eq. (18.24), we get

$$\Lambda' = \Lambda_\infty - (0.2289\Lambda_\infty + 60.32)\sqrt{c\alpha} \qquad (18.25)$$

Equation (18.25) allows us to find the true value of the degree of dissociation.

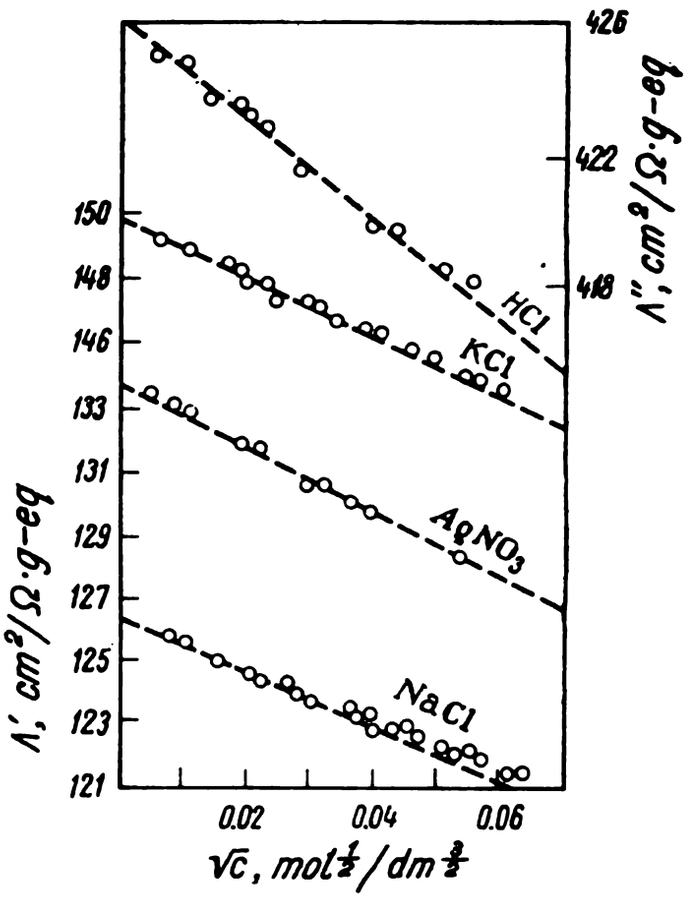



Fig. 18.2. Verification of Onsager's equation

**18.5. Calculation of Degree of Dissociation and Dissociation Constant for Weak Electrolytes.** Let us calculate the degree of dissociation and the dissociation constant for a weak electrolyte. We shall take acetic acid as an example, with consideration of the dependence of the mobility of the ions on their concentration (the ionic strength) and of the law of mass action.

D. MacInnes and T. Shedlovsky carefully measured the conductivity of solutions of $CH_3COOH$ and calculated their equivalent conductivity $\Lambda$. The limiting value $\Lambda_\infty$ was calculated from the limiting conductivities of HCl, NaCl and $CH_3COONa$ according to the Kohlrausch law [see Eq. (17.14)]:

$$\Lambda_\infty(CH_3COOH) = \Lambda_\infty(CH_3COONa) + \Lambda_\infty(HCl) - \Lambda_\infty(NaCl) \qquad (18.26)$$

and it was found that $\Lambda_\infty(CH_3COOH) = 390.75$.

The equivalent conductivity $\Lambda$ of a 0.002 414 $N$ solution of $CH_3COOH$ measured experimentally is equal to 32.21. According to the classical theory, we find the approximate value of the degree of dissociation by Eq. (18.16)

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{32.21}{390.75} = 0.082\,45$$

To precise the value of $\alpha$, we use Eq. (18.25), inserting into it the found values of $\Lambda_\infty$ and $\alpha$:

$$\Lambda' = 390.75 - (0.2289 \times 390.75 + 60.32)\sqrt{0.002\,414 \times 0.082\,45} = 388.59$$

$$\alpha' = \frac{\Lambda}{\Lambda'} = \frac{32.21}{388.59} = 0.082\,88$$

For further precising we find $\Lambda''$, introducing $\alpha'$ into Eq. (18.25) instead of $\alpha$:

$$\Lambda'' = 390.75 - (0.2289 \times 390.75 + 60.32)\sqrt{0.002\,414 \times 0.082\,88} = 388.58$$

$$\alpha'' = \frac{\Lambda}{\Lambda''} = \frac{32.21}{388.58} = 0.082\,88$$

In this case $\alpha$ is reproduced already after two substitutions. Sometimes three or four substitutions are required for this purpose.

After finding the true value of $\alpha$, we compute the dissociation function $k_c$ according to Eq. (18.12):

$$k_c = \frac{c\alpha^2}{1-\alpha} = \frac{0.002\,414 \times 0.082\,88^2}{0.917\,12} = 1.809 \times 10^{-5}$$

The values of $k_c$ computed in this way are given in Table 18.2.

In this way we calculate the final value of the true degree of dissociation if the activity coefficients are equal to unity. If the activity coefficients of ions and undissociated participants of a reaction are not equal to unity, the thermodynamic dissociation constant corresponding to equilibrium of the reaction $CH_3COOH + H_2O = CH_3COO^- + H_3O^+$ is expressed by the equation

$$K_{d,\,CH_3COOH} = \frac{c\alpha^2}{1-\alpha}\,\frac{f_\pm^2}{f} \tag{18.27}$$

where $f_\pm$ = mean ionic activity coefficient related to the volume concentration $c$

$f$ = activity coefficient of undissociated acid which for dilute solutions may be equated to unity.

To compute the value of $f_\pm$ for moderately dilute solutions, instead of the limiting Debye equation we use the Debye-Hückel equation (16.51):

$$\log f_\pm = -\frac{0.5092\sqrt{c\alpha}}{1+\sqrt{c\alpha}} \tag{18.28}$$

where $c\alpha = I$ is the ionic strength [see Eq. (16.51)].

Inserting the value of $f_{\pm}$ into Eq. (18.27), we get the final value of the dissociation constant of acetic acid (see Table 18.2).

The thermodynamic dissociation constant remains constant within the interval of values of $c$ from $3 \times 10^{-4}$ to $9 \times 10^{-2}$. At higher concentrations $K_d$ slowly decreases. This shows that Eqs. (18.25) and (18.28) are still insufficiently accurate. Knowing the mean value of the thermodynamic dissociation constant for dilute solutions $K_d = 1.752 \times 10^{-5}$, we can compute the degree of dissociation. For this purpose it is necessary to find the approximate value of $\alpha$ according to Eq. (18.27), considering $f_{\pm} = 1$. After this, inserting the found value of $\alpha$ and the value of the existing concentration $c$ into Eq. (18.28), we find $f_{\pm}$, insert it into Eq. (18.27), again determine $\alpha$, etc., until the results of repeated substitutions coincide.

**18.6. Acids and Bases.** The definitions of an acid as a substance capable of detaching hydrogen ions (hydroxonium) and of a base as a substance capable of detaching hydroxyl ions sufficiently well reflect the phenomena observed as long as we are dealing with aqueous solutions. In other solvents such as ether, benzene and nitrocompounds these definitions can no longer be considered accurate. On the basis of investigations mainly relating to the catalytic action of acids and bases, J. Brönsted and T. Lowry proposed new definitions, namely, *a substance capable of giving up a proton is called an acid, and a substance capable of attaching a proton is called a base, i.e. an acid and a base are related by the equation*

$$\text{Acid (A)} = \text{Proton } (H^+) + \text{Base (B)} \tag{18.29}$$

The acid and the base entering into this equation are called a a *conjugate* acid-base pair. As will be shown below, protons may detach themselves from particles carrying a positive charge, from neutral particles and even from negatively charged particles (for example, in the multistep dissociation of acids). The charge of a base correspondingly differs.

It was noted above that the probability of free protons existing in solutions is very low. For this reason the protons given up by an acid should attach themselves to molecules of the solvent. If the molecules of the solvent are not capable either of attaching protons or of detaching them, the solute cannot display the properties of an acid or a base. In other words, a substance can display acid properties only when the solvent has basic properties, i.e. if we can write that

$$\underset{\text{Acid}}{A_1} + \underset{\text{Base}}{B_2} = \underset{\text{Base}}{B_1} + \underset{\text{Acid}}{A_2} \tag{18.30}$$

Substance $A_1$ loses a proton and transforms into base $B_1$, and substance $B_2$ attaches a proton and changes into acid $A_2$. The pairs $A_1$-$B_1$ and $B_2$-$A_2$ are conjugate acid-base pairs.

If the solvent attaches a proton, i.e. has the properties of a base, it is called *protophilic*. A solvent giving up a proton, i.e. having acid properties, is called *protogenic* (or *protophobic*). Protophilic solvents include water, alcohols, acetone, ethers, liquid ammonia, amines and to a certain extent formic and acetic acids. Protogenic solvents also include water and alcohols, but the most typical are pure acids (acetic, sulphuric, formic), and also liquid hydrogen chloride and hydrogen fluoride. Solvents capable of either detaching or attaching a proton are called *amphoprotic* (or *amphoteric*). Solvents that are capable of neither detaching nor attaching a proton (for example, benzene) are called *aprotic*.

A solution of an acid in water is thus a system in which equilibrium exists between two conjugate acid-base pairs, namely,

$$\underset{\text{Acid}}{AH} + \underset{\text{Base}}{H_2O} \rightleftarrows \underset{\text{Base}}{A^-} + \underset{\text{Acid}}{H_3O^+} \qquad (18.31)$$

(the first pair is AH and $A^-$, the second pair is $H_2O$ and $H_3O^+$).

Similar equilibrium exists in a solution of a base in water. For example,

$$\underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{H_2O} \rightleftarrows \underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{OH^-} \qquad (18.32)$$

(the first pair is $NH_3$ and $NH_4^+$, the second pair is $H_2O$ and $OH^-$). It follows from Eqs. (18.31) and (18.32) that with such a method of classification not only molecules, but also ions must be classified as acids or bases.

Water is a very strong protophilic solvent. For this reason many so-called strong acids completely or almost completely give up their protons to water. The same acids when dissolved in a less protophilic solvent form equilibrium systems in which the acid dissociates only partly. Such solvents, for example acetic acid, make it possible to compare the relative strength of acids which completely dissociate in water. The following sequence is obtained:

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

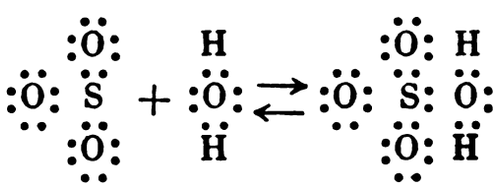
All the acids of the series given above are weak in acetic acid, the weakest being nitric acid. The same sequence remains when comparing the strengths of acids determined by the potentiometric method or according to the catalytic activity. Although the degree of dissociation of the acids listed above in acetic acid is not great, the solvated hydrogen ions $CH_3COOH_2^+$ formed have an exceedingly great activity. Acetic acid, being protogenic, very actively tends to give up the proton attached to it. This is why the ion $CH_3COOH_2^+$ reacts like an exceedingly strong acid. The high acidity of such ions can be established with the aid of a hydrogen electrode, and also according to their catalytic activity. Solutions containing ions of the $CH_3COOH_2^+$ type are called *superacidic* ones.

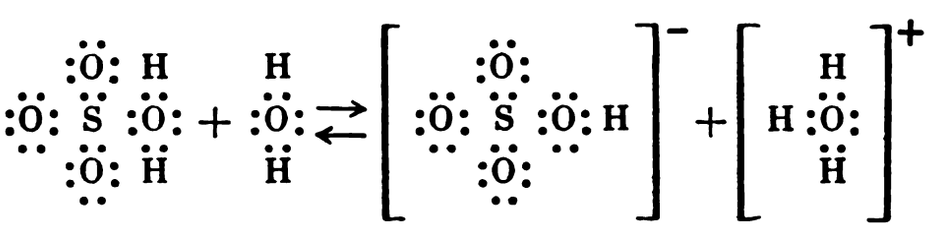
Thus the same acid, depending on the properties of the solvent, may be either weak or strong. This also holds for solutions of bases. The greater the protogenic nature of a solvent, the stronger is a base in its solution. Reactions involving the transition of protons are called *protolytic*.

Brönsted's theory of acids and bases, however, does not cover a great variety of compounds that are not capable of detaching or attaching protons, but that have clearly expressed features of acids and bases.

Several theories have been developed that allow us to approach the concepts "acid" and "base" more comprehensively. Below we shall consider the electronic theory of acids proposed by G. Lewis and the aprotic theory of M. Usanovich.

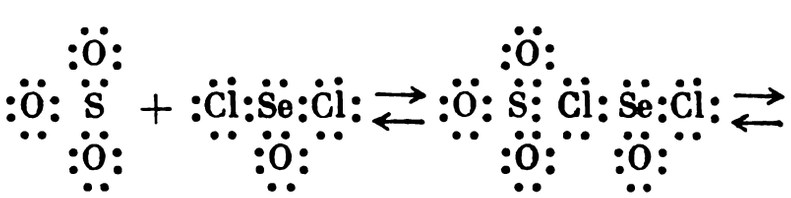
The main postulate of Lewis's theory consists in the fact that acid-base processes cannot consist only in the transfer of a proton. According to Lewis, *an acid is a substance that can accept an electron pair from some other molecule to complete its stable quota of electrons, usually an octet. A base is a substance that can share such a pair of electrons with some other atom to complete the stable quota of electrons of the latter.* Thus any equilibrium satisfying this feature should be considered as acid-base equilibrium. For example, in the interaction of $SO_3$ and $H_2O$ the water is a base, since it has a free pair of electrons, while the sulphuric anhydride, which can interact with water accepting this pair of electrons, is an acid.

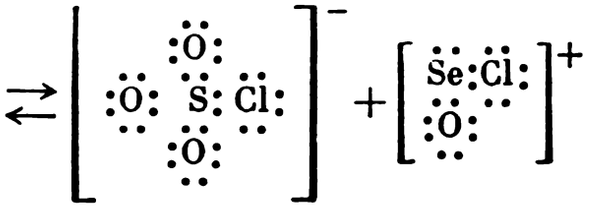




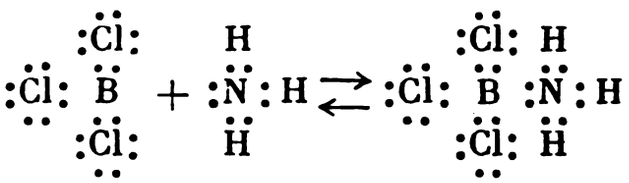
The sulphuric acid formed may dissociate as shown above, and also with the formation of two ions $H_3O^+$ and $SO_4^{2-}$.

A similar compound sharing a pair of electrons may also form and then dissociate into ions without the participation of hydrogen. For example, this occurs in the reaction of selenium oxychloride $SeOCl_2$, which in the given case is a base, and sulphuric anhydride $SO_3$, which is an acid, namely,

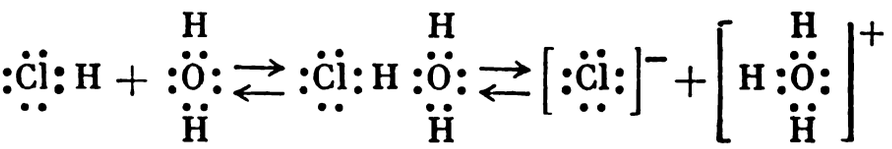




From the viewpoint of Lewis, dissociation of the product into ions is not an essential feature of acid-base interaction. For example, boron trichloride (an acid) and ammonia (a base) react to form a product that does not decompose into ions:



It should be noted, however, that Lewis's theory is not always confirmed by experimental data. Thus, according to Lewis hydrogen chloride should dissociate in water according to the scheme



But according to quantum mechanics hydrogen cannot have four electrons in its outer shell.

I. Kolthoff proposed to change the terminology and combine the Brönsted and Lewis theories, retaining the Brönsted definition of an acid as a substance consisting of a proton (or several protons) and a base.

Kolthoff considered substances that according to Lewis are acids as *acceptors of electron pairs*. Such acceptors include $H^+$, $BCl_3$ and $SO_3$. They were called *protoacids*. Kolthoff proposed to consider Brönsted's double protolytic equilibrium

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

as the transition of a proton from a weak base ($Cl^-$) to a stronger one ($H_2O$) without the formation of an intermediate. Brönsted's acids are thus products of neutralization of bases by protons.

Lewis established that the relative strength of protoacids, in contrast to protonic acids, depends not only on the solvent, but also on the base taken for comparison, i.e. participating in reactions with a number of acids.

Lewis's theory (1938-1939) is based on the assumption that the essence of chemical interaction consists in the formation of electron octets around atoms. This theory is not universal, however, since at present a great number of cases are known when the formation of a compound is not connected with the formation of a stable octet

configuration of the electrons. It should be stressed that any classification based on a certain mechanism of formation of compounds inevitably changes with the development of our ideas of the structure of the atom and the nature of the chemical bond.

M. Usanovich starts from the assumption that every process resulting in the formation of a salt is an acid-base one, and since not only substances containing hydrogen can participate in the formation of salts, aprotic acids are also possible. According to Usanovich *acids are substances capable of giving up cations or attaching anions (and also electrons); bases, correspondingly, are substances capable of attaching cations or giving up anions.* For example, in the reaction

$$Na_2O + SiO_2 \rightleftarrows 2Na^+ + SiO_3^{2-}$$

$Na_2O$ is a base, since it gives up the anion $O^{2-}$, and $SiO_2$ is an acid, since it attaches this anion. Let us consider the reactions

$$N(CH_3)_3 + HI \rightleftarrows N(CH_3)_3H^+ + I^-$$
$$N(CH_3)_2H + CH_3I \rightleftarrows N(CH_3)_3H^+ + I^-$$

According to Usanovich, both HI and $CH_3I$ are acids, since both compounds give up a cation, which is attached to the corresponding base [$N(CH_3)_3$ or $N(CH_3)_2H$], yielding the same products in both cases, namely, the acid $N(CH_3)_3H^+$ and the base $I^-$.

Thus the definitions of a base given by Usanovich and Brönsted coincide. According to Brönsted, a base is a compound capable of attaching a proton, but such substances can usually also attach various other cations, which is indicated by Usanovich. Their definitions of an acid, however, do not coincide. According to Brönsted, an acid is a substance giving up a proton, while according to Usanovich an acid is a substance giving up any cation, and not only a proton, or attaching an anion (including an electron). Thus, in the reaction

$$2Na + Cl_2 \rightleftarrows 2Na^+ + 2Cl^-$$

the chlorine is an acid, since it attaches an electron, and the sodium is a base, since it gives up this electron. Reasoning in the same way, we can say that the sodium ion formed is an acid, and the chloride ion a base.

Consequently, Usanovich's formulation of acid-base reactions includes reactions of salt formation, oxidation and reduction reactions and exchange reactions. The classification is so broad that it covers all the classes of chemical compounds, since any chemical reaction is accompanied by the transfer of electrons. Usanovich does not separate a class of acids and bases as we usually understand it. Moreover, his initial definitions themselves have a certain lack of clarity. For example, sodium produces the cation $Na^+$ and an electron, i.e. it can be related on equal grounds to acids and to bases.

Hence the concepts "acid" and "base" are relative. The too general nature of Usanovich's classification makes it very inconvenient for investigating acids and bases in the usual understanding of these terms.

**18.7. Protolytic Equilibrium.** The decomposition of an acid into a proton and the conjugate base, like any other reaction, tends to equilibrium. For the decomposition of acetic acid, for example

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

the equilibrium constant can be written as follows:

$$K_{CH_3COOH} = \frac{a_{CH_3COO^-}}{a_{CH_3COOH}} a_{H^+} \tag{18.33}$$

The quantity $K_{CH_3COOH}$ is called the *true thermodynamic constant of dissociation* of this acid into a free proton and a base, or the *acidity constant*. It should never be confused with the thermodynamic equilibrium constant of acetic acid with hydroxonium and a base.

The main part of the protons given up by an acid are attached to other molecules playing the part of a base. If the acid is dissolved in water, the following reaction proceeds:

$$H^+ + H_2O = H_3O^+$$

in which $H_3O^+$ plays the part of an acid, and $H_2O$ of a base. The true thermodynamic dissociation constant for the ion $H_3O^+$ is

$$K_{H_3O^+} = \frac{a_{H_2O}}{a_{H_3O^+}} a_{H^+} \tag{18.34}$$

Dividing Eq. (18.33) by Eq. (18.34), we get

$$\frac{K_{CH_3COOH}}{K_{H_3O^+}} = \frac{a_{CH_3COO^-} a_{H_3O^+}}{a_{CH_3COOH} a_{H_2O}} = K_a \tag{18.35}$$

where $K_a$ is the equilibrium constant of the reaction

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Knowing $K_a$, we can find the thermodynamic dissociation constant for acetic acid in an aqueous solution $K_{d,\,CH_3COOH}$. This constant can be found on the basis of experimental data.

Equation (18.35) shows that two opposite processes proceed in the dissociation of acetic acid. On one hand, the acetic acid tends to give up a proton to the water, and on the other, the ion $H_3O^+$ tends to return a proton to the ion $CH_3COO^-$. The constant shows how many times the first acid is stronger than the second one. It is this ratio that interests us first of all in appraising the strength of acids.

To calculate the values of $K_a$ it is necessary that values of the true thermodynamic dissociation constants for various substances be available. To compile such a summary table we have at our disposal only Eq. (18.35). It can be used only if we know at least one true thermodynamic dissociation constant. Since we cannot find the actual value of any $K$, we have to assume a certain arbitrary value of one of the true thermodynamic dissociation constants. This value, therefore, is the product of the true constant and a certain unknown factor. Now all the other constants acquire a quite definite value, having, however, nothing in common with their actual value, since every time it is equal to the product of the actual constant $K$ and the same unknown factor. But since we do not have the aim of determining the activity of a proton, the absolute values of the true thermodynamic dissociation constants are not necessary, and the unknown factor, which enters into both the numerator and the denominator of Eq. (18.35), does not influence the value of the ratio.

This circumstance makes it possible to select the true thermodynamic dissociation constant of the ion $H_3O^+$ as the starting point. Its value is very important to know in studying aqueous solutions. To simplify calculations we assume that $K_{H_3O^+}$ is equal to 55.5. The use of this value of the constant in Eq. (18.35) yields

$$\frac{K_{CH_3COOH}}{55.5} = \frac{a_{CH_3COO^-} a_{H_3O^+}}{a_{CH_3COOH} a_{H_2O}} \tag{18.36}$$

For dilute solutions

$$a_{H_2O} = [H_2O] = 55.5 \text{ mol/dm}^3$$

Inserting this value into Eq. (18.36), we get

$$K_{CH_3COOH} = K_{d,\,CH_3COOH} = \frac{a_{CH_3COO^-} a_{H_3O^+}}{a_{CH_3COOH}} \tag{18.37}$$

i.e. at the value of the constant $K_{H_3O^+}$ that we have selected the true thermodynamic dissociation constant of acetic acid is equal to its thermodynamic dissociation constant. This naturally also holds for the true thermodynamic dissociation constants of all other acids when their dissociation in an aqueous medium is considered. Table 18.3 gives the dissociation constants for various compounds capable of detaching a proton.

These constants, as indicated above, are numerically equal to the corresponding thermodynamic dissociation constants.

Knowing the true thermodynamic dissociation constants, we can easily and simply find the constants characterizing ionic equilibria. Let us consider, for example, the dissociation of water, consisting in that one molecule gives up a proton and another one attaches this proton. Thus water is simultaneously an acid and a base:

$$H_2O + H_2O = OH^- + H_3O^+$$

TABLE 18.3
**True Thermodynamic Constants of Dissociation in Aqueous Solutions at 18 °C**
(Acidity Constants)

| Acid | Base | $K$ | Acid | Base | $K$ |
|---|---|---|---|---|---|
| $H_3O^+$ | $H_2O$ | 55.5 | $H_3BO_3$ | $H_2BO_3^-$ | $6\times10^{-10}$ |
| $H_2O$ | $OH^-$ | $1.33\times10^{-16}$ | $NH_4^+$ | $NH_3$ | $4.14\times10^{-10}$ |
| $H_2S$ | $HS^-$ | $8\times10^{-8}$ | $Al(H_2O)_6^{3+}$ | $Al(H_2O)_5OH^{2+}$ | $1.3\times10^{-5}$ |
| $HS^-$ | $HS^{2-}$ | $2\times10^{-15}$ | $Fe(H_2O)_6^{3+}$ | $Fe(H_2O)_5OH^{2+}$ | $6.3\times10^{-3}$ |
| $H_2SO_3$ | $HSO_3^-$ | $1.7\times10^{-2}$ | $HCOOH$ | $HCOO^-$ | $2.1\times10^{-4}$ |
| $HSO_3^-$ | $SO_3^{2-}$ | $5\times10^{-6}$ | $CH_3COOH$ | $CH_3COO^-$ | $1.8\times10^{-5}$ |
| $H_2SO_4$ | $SO_4^{2-}$ | $2\times10^{-2}$ | $CH_2ClCOOH$ | $CH_2ClCOO^-$ | $1.4\times10^{-3}$ |
| $H_3PO_4$ | $H_2PO_4^-$ | $7.6\times10^{-3}$ | $CHCl_2COOH$ | $CHCl_2COO^-$ | $5.5\times10^{-2}$ |
| $H_2PO_4^-$ | $HPO_4^{2-}$ | $5.9\times10^{-8}$ | $COOHCOOH$ | $COOHCOO^-$ | $5.7\times10^{-2}$ |
| $HPO_4^{2-}$ | $PO_4^{3-}$ | $3.5\times10^{-13}$ | $COOHCOO^-$ | $-COOCOO^-$ | $6.8\times10^{-5}$ |
| $H_2CO_3$ | $HCO_3^-$ | $4.3\times10^{-7}$ | $CH_3NH_3^+$ | $CH_3NH_2$ | $1.6\times10^{-11}$ |
| $HCO_3^-$ | $CO_3^{2-}$ | $4.7\times10^{-11}$ | $(CH_3)_2NH_2^+$ | $(CH_3)_2NH$ | $1.2\times10^{-11}$ |
| $HCN$ | $CN^-$ | $7\times10^{-10}$ | | | |

Equilibrium sets in in the solution, and its constant is equal to the ratio of the true thermodynamic dissociation constants or, which is the same, to the ratio of the thermodynamic dissociation constants $K_d$. Let us write the reactions of dissociation of water and of dissociation of hydroxonium. In both cases dissociation proceeds with the participation of one molecule of water that attaches a proton:

$$H_2O + H_2O = OH^- + H_3O^+ \text{ and } H_3O^+ + H_2O = H_2O + H_3O^+$$

The thermodynamic dissociation constants are correspondingly expressed by the equations

$$K_{d,\,H_2O} = \frac{a_{OH^-}a_{H_3O^+}}{a_{H_2O}} \quad \text{and} \quad K_{d,\,H_3O^+} = \frac{a_{H_2O}a_{H_3O^+}}{a_{H_3O^+}} = a_{H_2O} \tag{18.38}$$

Division of the first constant by the second one yields

$$K_a = \frac{K_{d,\,H_2O}}{K_{d,\,H_3O^+}} = \frac{K_{H_2O}}{K_{H_3O^+}} = \frac{a_{OH^-}a_{H_3O^+}}{a_{H_2O}^2} \tag{18.39}$$

For pure water $a_{H_2O} = [H_2O] = 55.5$. Since $K_{H_3O^+}$ has been taken equal to 55.5 (see above), Eq. (18.39) becomes

$$K_{H_2O} = \frac{a_{OH^-}a_{H_3O^+}}{a_{H_2O}}$$

or

$$K_{H_2O}a_{H_2O} = a_{OH^-}a_{H_3O^+} \tag{18.40}$$

At 18 °C (see Table 18.3)

$$a_{OH^-}a_{H_3O^+} = K_{H_2O}a_{H_2O} = 1.33 \times 10^{-16} \times 55.5 = 0.74 \times 10^{-14}$$

Thus the product $K_{H_2O}a_{H_2O}$ is the ionic product of water $K_w$ (Table 18.4):

$$K_w = a_{OH^-}a_{H_3O^+}$$

In all aqueous solutions equilibrium so sets in that Eq. (18.6) is obeyed. The following equation holds for the most dilute solutions[1]

$$K_w = k_w = [H_3O^+]\,[OH^-] \tag{18.41}$$

i.e. the product of the activities of the ions $K_w$ is equal to the product of the concentrations of the ions $k_w$.

TABLE 18.4

**Ionic Product of Water Found from Measurements of E.M.F. of Cells Containing Various Halides, and from Conductivity of Water**

| Temperature, °C | $K_w \times 10^4$ found by measuring e.m.f. | | | | Mean value of $K_w \times 10^{14}$ | $K_w \times 10^{14}$ found from conductivity of water |
|---|---|---|---|---|---|---|
| | NaCl | KCl | LiCl | $BaCl_2$ | | |
| 0 | 0.113 | 0.115 | 0.113 | 0.112 | 0.114 | 0.13 |
| 10 | 0.292 | 0.293 | 0.292 | 0.280 | 0.292 | 0.36 |
| 20 | 0.681 | 0.681 | 0.681 | 0.681 | 0.681 | 0.86 |
| 25 | 1.007 | 1.008 | 1.007 | 1.009 | 1.008 | 1.27 |
| 30 | 1.470 | 1.471 | 1.467 | 1.466 | 1.468 | 1.89 |
| 40 | 2.914 | 2.916 | — | 2.920 | 2.917 | 3.8 |
| 50 | 5.482 | 5.476 | — | 5.465 | 5.474 | 5.6 |
| 100 | — | — | — | — | — | 74 |

As a second example let us find the dissociation constant for a base dissolved in water. In dissolving in water ammonia reacts with it according to the equation

$$NH_3 + H_2O = NH_4^+ + OH^- \tag{18.42}$$

The equilibrium constant for this reaction

$$K_a = \frac{a_{NH_4^+}a_{OH^-}}{a_{NH_3}a_{H_2O}} \tag{18.43}$$

[1] For concentrated solutions of electrolytes the product $[H_3O^+][OH^-]$ depends on the ionic strength of the solution.

For the calculation of the dependence of $[H_3O^+][OH^-] = K_w/f_{H_3O^+}f_{OH^-}$ on $I$ see Sec. 16.7.

But $a_{H_2O}$ for dilute solutions may be considered a constant quantity. Hence, combining $K_a$ and $a_{H_2O}$, we get the equation

$$K_{d,\,NH_3}=\frac{a_{NH_4^+}a_{OH^-}}{a_{NH_3}} \tag{18.44}$$

where $K_{d.\,NH_3}$ is the thermodynamic dissociation constant of the base. For infinitely dilute solutions the activities can be replaced by the concentrations.

Having at our disposal a table of the true thermodynamic dissociation constants, we can easily compute the dissociation constant for the base. Using Eq. (18.42), we write

$$K_{d,\,H_2O}=\frac{a_{OH^-}a_{H_3O^+}}{a_{H_2O}} \quad \text{and} \quad K_{d,\,NH_4^+}=\frac{a_{NH_3}a_{H_3O^+}}{a_{NH_4^+}} \tag{18.45}$$

$K_{d.H_2O}$ relates to the forward reaction, and $K_{d.\,NH_4^+}$ to the reverse one. Dividing the first equation by the second one, we have

$$\frac{K_{d,\,H_2O}}{K_{d,\,NH_4^+}}=\frac{a_{OH^-}a_{NH_4^+}}{a_{H_2O}a_{NH_3}}$$

Transferring $a_{H_2O}$ from the right-hand part to the left-hand one and using Eqs. (18.6), (18.40), (18.44) and Table 18.3, we find

$$K_{d,\,NH_3}=\frac{K_w}{K_{d,\,NH_4^+}}=\frac{0.74\times10^{-14}}{4.14\times10^{-10}}=1.79\times10^{-5}$$

When considering solutions in a solvent other than $H_2O$ it is necessary to compile a similar table of the true thermodynamic dissociation constants for this solvent. A different value is naturally taken for the true thermodynamic dissociation constant of the solvent itself.

**18.8. Hydrolysis.** In the previous sections we considered the interaction of acids and bases with the water which they are dissolved in. The result of this interaction is dissociation of the acid or base. In the present section we shall deal with the interaction with water of salts dissolved in it.

Let us consider, for example, NaCl, a salt of the strong, i.e. highly protogenic, acid HCl, which easily gives up a hydrogen ion, and the strong, i.e. highly protophilic, base NaOH, whose hydroxyl energetically binds the hydrogen ion. In an aqueous solution of NaCl the ions $H^+$ and $OH^-$ are sufficiently strongly bound to each other, and the concentrations $[H_3O^+]$ and $[OH^-]$ are not great, since they are determined by the ionic product of water.

Different relations are observed in aqueous solutions of the salts of a weak acid and a strong base or, conversely, a strong acid and a weak base. In studving these systems we shall consider only the

laws holding for very dilute solutions, for which the activities may be replaced by the concentrations.

Let us consider the salt of a weak acid and a strong base, for example $CH_3COONa$. If the solution of this salt is sufficiently dilute, it can be considered that the salt is completely dissociated. But it is owing to the fact that acetic acid is weak that the ion $CH_3COO^-$ displays basic properties, i.e. it is capable of attaching a proton with sufficient strength. As a result of interaction of this ion with water equilibrium sets in:

$$CH_3COO^- + H_2O = CH_3COOH + OH^- \tag{18.46}$$

Reaction (18.46) is an example of a *reaction of hydrolysis*, i.e. exchange decomposition with water. Using the law of mass action, we get

$$K_a = \frac{a_{CH_3COOH} a_{OH^-}}{a_{CH_3COO^-} a_{H_2O}}$$

For dilute solutions the quantity $a_{H_2O}$ may be considered constant. By transferring it to the left-hand side and denoting $K_a a_{H_2O}$ by $K_{hydr}$—the *hydrolysis constant*—we have

$$K_{hydr} = \frac{a_{CH_3COOH} a_{OH^-}}{a_{CH_3COO^-}} \tag{18.47}$$

For dilute solutions we may write

$$K_{hydr,\, CH_3COO^-} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \tag{18.48}$$

where $K_{hydr,\, CH_3COO^-}$ is the approximate hydrolysis constant expressed through the concentrations.

Thus a solution of the salt of a weak acid and a strong base is found to be alkaline as a result of hydrolysis. The ratio of the concentration of the hydroxyl formed to the initial concentration of the salt is called the *degree of hydrolysis* or the *fraction hydrolyzed* and is denoted by $\beta$:

$$\beta = \frac{[OH^-]}{[CH_3COONa]} \tag{18.49}$$

The quantity $[CH_3COONa]$ may be replaced by $[Na^+]$, since the salt is completely dissociated and the concentration of the ion of a strong base at any fraction hydrolyzed remains constant. This ion does not participate in the reaction of hydrolysis.

The same relations hold in a solution of a salt of a weak base and a strong acid, only the acid and the base exchange their roles. Let us consider as an example a dilute solution of ammonium chloride in water. The dissolved salt practically completely dissociates. The

ion $NH_4^+$ reacts with the water according to the equation

$$NH_4^+ + H_2O = NH_3 + H_3O^+ \tag{18.50}$$

Repeating the reasoning accompanying the transition from Eq. (18.46) to Eqs. (18.47) and (18.48), we get

$$K_{\text{hydr, } NH_4^+} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \tag{18.51}$$

Let us find the relation between the hydrolysis constant $K_{\text{hydr}}$ and the fraction hydrolyzed $\beta$ for a binary mono-monovalent electrolyte. Let us denote the total concentration of the salt, for example $CH_3COONa$, by $c$. Then $[OH^-] = [CH_3COOH] = c\beta$ and $[CH_3COO^-] = c(1 - \beta)$, whence

$$K_{\text{hydr}} = \frac{c^2\beta^2}{c(1-\beta)} = \frac{c\beta^2}{1-\beta}$$

Hence, knowing $K_{\text{hydr}}$ and $c$, we can calculate the fraction hydrolyzed. The same formula is obtained for the hydrolysis of $NH_4Cl$.

We can use the quantities $k_w$ and $k_c$ to compute $K_{\text{hydr}}$. Indeed, multiplying the numerator and denominator of Eq. (18.48) by $[H_3O^+]$ and of Eq. (18.51) by $[OH^-]$, we get

$$K_{\text{hydr, } CH_3COO^-} = \frac{[CH_3COOH][OH^-][H_3O^+]}{[CH_3COO^-][H_3O^+]}$$

$$K_{\text{hydr, } NH_4^+} = \frac{[NH_3][H_3O^+][OH^-]}{[NH_4^+][OH^-]} \tag{18.52}$$

and according to Eqs. (18.37) and (18.41), for $CH_3COONa$ and $NH_4Cl$ we have, respectively,

$$K_{\text{hydr, } CH_3COO^-} = \frac{k_w}{k_{CH_3COOH}} \quad \text{and} \quad K_{\text{hydr, } NH_4^+} = \frac{k_w}{k_{NH_4OH}} \tag{18.53}$$

We can also find the hydrolysis constant by using the acidity constants (true thermodynamic dissociation constants). On the basis of an equation of hydrolysis of the type of Eq. (18.46) we can write for acids, i.e. for substances giving up $H^+$

$$K_{H_2O} = \frac{a_{OH^-}}{a_{H_2O}} a_{H^+} \quad \text{and} \quad K_{CH_3COOH} = \frac{a_{CH_3COO^-} a_{H^+}}{a_{CH_3COOH}}$$

Division of the first equation by the second one and transferring of $a_{H_2O}$ to the left-hand side yield

$$\frac{K_{H_2O} a_{H_2O}}{K_{CH_3COOH}} = \frac{a_{OH^-} a_{CH_3COOH}}{a_{CH_3COO^-}} = K_{\text{hydr, } CH_3COO^-} \tag{18.54}$$

To calculate $K_{hydr}$ for a weak base we repeat the same reasoning on the basis of Eq. (18.50):

$$K_{NH_4^+} = \frac{a_{NH_3}}{a_{NH_4^+}} a_{H^+}$$

$$K_{H_3O^+} = \frac{a_{H_2O}}{a_{H_3O^+}} a_{H^+}$$

$$\frac{K_{NH_4^+} a_{H_2O}}{K_{H_3O^+}} = \frac{a_{NH_3} a_{H_3O^+}}{a_{NH_4^+}} = K_{hydr,\, NH_4^+}$$

But according to Eq. (18.38)

$$K_{H_3O^+} = a_{H_2O}, \quad \text{whence} \quad K_{hydr,\, NH_4^+} = K_{NH_4^+}$$

It should be noted that in all the examples we considered the simplest case when the electrolyte decomposed into two ions. When it decomposes into three or more ions the equations correspondingly become more complicated.

The fraction hydrolyzed $\beta$ is usually much smaller than unity. Hence the expression for the hydrolysis constant can be simplified. Instead of $K_{hydr} = c\,\frac{\beta^2}{1-\beta}$ we can use the expression $K_{hydr} = c\beta^2$, whence

$$\beta = \sqrt{\frac{K_{hydr}}{c}} \tag{18.55}$$

This equation shows that if the fraction hydrolyzed is small it is directly proportional to the square root of the hydrolysis constant and inversely proportional to the square root of the concentration. Table 18.5 gives examples of the dependence of the fraction hydrolyzed $\beta$ on the value of $K_{hydr}$ and the concentration of a solution of an electrolyte decomposing into two monovalent ions.

TABLE 18.5

**Fraction of Salts of Weak Acids and Strong Bases Hydrolyzed at 25 °C**

| $k_c$ | $K_{hydr}$ | Fraction hydrolyzed $\beta$ at concentrations of | | | |
|---|---|---|---|---|---|
| | | 0.001 *N* | 0.01 *N* | 0.1 *N* | 1 *N* |
| $10^{-4}$ | $10^{-10}$ | $3.3 \times 10^{-4}$ | $10^{-4}$ | $3.2 \times 10^{-5}$ | $10^{-5}$ |
| $10^{-6}$ | $10^{-8}$ | $3.2 \times 10^{-3}$ | $10^{-3}$ | $3.2 \times 10^{-4}$ | $10^{-4}$ |
| $10^{-8}$ | $10^{-6}$ | $3.2 \times 10^{-2}$ | $10^{-2}$ | $3.2 \times 10^{-3}$ | $10^{-3}$ |
| $10^{-10}$ | $10^{-4}$ | 0.27 | 0.095 | $3.2 \times 10^{-2}$ | $10^{-2}$ |

To establish the temperature dependence of the hydrolysis constant, let us consider Eqs. (18.53). The ionic product of water grows 500 times when the temperature changes from 0 to 100 °C, while the dissociation constants do not practically depend on the temperature (see Table 18.1). The hydrolysis constants therefore grow with the temperature. The fraction hydrolyzed β grows correspondingly.

When a salt of a weak acid and a weak base, for example $CH_3COONH_4$, which we shall denote $AcNH_4$, is dissolved in water, the salt dissociates almost completely into the ions $Ac^-$ and $NH_4^+$, each of which participates in hydrolytic equilibrium, namely,

$$Ac^- + H_2O = AcH + OH^-$$

$$NH_4^+ + H_2O = NH_3 + H_3O^+$$

Summation of these equations gives the complete equation of hydrolytic equilibrium:

$$NH_4^+ + Ac^- + 2H_2O = NH_3 + AcH + H_3O^+ + OH^- \qquad (18.56)$$

In addition to hydrolytic equilibrium, there is equilibrium between the ions $H_3O^+$ and $OH^-$ and the undissociated water in the solution:

$$2H_2O = H_3O^+ + OH^- \qquad (18.57)$$

Subtracting Eq. (18.57) from Eq. (18.56), we get

$$NH_4^+ + Ac^- = NH_3 + AcH$$

or in the general case, if we denote a base by B and an acid by HA, we have

$$BH^+ + A^- = B + HA$$

whence, according to the law of mass action, the hydrolysis constant

$$K_{hydr} = \frac{a_B a_{HA}}{a_{BH^+} a_{A^-}} \qquad (18.58)$$

Multiplication of the numerator and denominator by $a_{H_3O^+} a_{OH^-}$ gives

$$K_{hydr} = \frac{a_B a_{HA} a_{H_3O^+} a_{OH^-}}{a_{BH^+} a_{A^-} a_{H_3O^+} a_{OH^-}} = \frac{K_w}{K_{d,HA} K_{d,B}} \qquad (18.59)$$

The activity coefficients of all the substances in Eq. (18.58) may be considered equal to unity for dilute solutions. Hence Eq. (18.58) becomes

$$K_{hydr} = \frac{c_B c_{HA}}{c_{BH^+} c_{A^-}} = \frac{k_w}{k_{HA} k_B} \qquad (18.60)$$

If the initial concentration of the salt is $c$ mol/dm³, and the fraction hydrolyzed is β, then (considering that the salt is completely dissociated) the quantities $c_{HA}$ and $c_B$ can be assumed equal to $c\beta$ and the quantities $c_{A^-}$ and $c_{BH^+}$ equal to $c(1-\beta)$—the concentration

of the unhydrolyzed salt Using these values in Eq. (18.60), we get

$$K_{hydr} = \frac{\beta^2}{(1-\beta)^2} \tag{18.61}$$

whence

$$\beta = \frac{\sqrt{K_{hydr}}}{1+\sqrt{K_{hydr}}}$$

If $K_{hydr}$ is small in comparison with unity, then neglecting $\sqrt{K_{hydr}}$ in the denominator, we have

$$\beta = \sqrt{K_{hydr}}$$

or, using the value of $K_{hydr}$ from the approximate equation (18.60):

$$\beta = \sqrt{\frac{k_w}{k_{HA}k_B}} \tag{18.62}$$

According to this equation, which has been obtained on the basis of approximate equations, the fraction of the salt of a weak acid and a weak base hydrolyzed does not depend on the concentration of this salt in the solution.

**18.9. Dissociation Constants for Polybasic Acids.** A polybasic acid dissociates in steps, a special dissociation constant corresponding to the detachment of each hydrogen ion. If the first hydrogen ion is detached from an acid residue carrying only one charge, the second one is detached from an acid residue carrying two charges, etc. A greater and greater energy is required to detach each subsequent hydrogen ion, and the dissociation constant decreases accordingly.

Thus, in the dissociation of phosphoric acid at $t = 18$ °C we have

$$H_3PO_4 + H_2O = H_3O^+ + H_2PO_4^-; \quad K_d^{I} = \frac{a_{H_2PO_4^-}a_{H_3O^+}}{a_{H_3PO_4}} = 7.6 \times 10^{-3}$$

$$H_2PO_4^- + H_2O = H_3O^+ + HPO_4^{2-}; \quad K_d^{II} = \frac{a_{HPO_4^{2-}}a_{H_3O^+}}{a_{H_2PO_4^-}} = 5.9 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O = H_3O^+ + PO_4^{3-}; \quad K_d^{III} = \frac{a_{PO_4^{3-}}a_{H_3O^+}}{a_{HPO_4^{2-}}} = 3.5 \times 10^{-13}$$

If $K_d^{I} \gg K_d^{II}$, then in determining $K_d^{I}$ the acid can be considered as a monobasic one and the methods that are applicable to monobasic acids can be used. If $K_d^{I}/K_d^{II} < 10^3$, the second step can no longer be neglected. In this case the transport numbers are used for calculating the dissociation constants. These numbers are used to find the numbers of ions with different charges transferred. It was found by this method that the first step in the dissociation of sulphuric acid is entirely completed even at high concentrations. For the second step of dissociation of this acid $K_d^{II} = 0.01$. At a concentration

of the acid of $c = 0.1$ a value of $\alpha$ equal to 0.62 corresponds to this value of the constant. Thus $H_2SO_4$ is also a quite strong acid in the second step of dissociation. The concentration of $SO_4^{2-}$, however, nevertheless depends on the concentration of the acid.

**18.10. Hydrogen Ion Exponent (pH).** To simplify the way of expressing the concentration of hydrogen ions, S. Sorensen in 1909 introduced a quantity that is the logarithm of the hydrogen ion concentration taken with the reverse sign. This quantity is called the *hydrogen ion exponent* or pH

$$pH = -\log [H^+] \tag{18.63}$$

The pH of various solutions and media are being investigated at present very thoroughly in a multitude of branches of the natural sciences, since it has a very great significance both in solving scientific problems and in developing technical processes in the most diverse branches of the national economy. The pH is a most important characteristic of biological processes. In medicine it serves to discover pathological deviations from normal, in agriculture it is used to characterize the acidity of soils, the drought- and frost-resistance of plants, etc. The pH has an exceedingly great importance for hydrogeological processes in the upper layers of the Earth's crust and on its surface. The pH is used to standardize and control production in the food, medicine, paper, textile, petroleum and other branches of industry. In the automation of production processes the measurement of the pH of solutions is frequently used as the starting point for designing regulators.

Standard solutions of acids serving as prototypes are used to determine the hydrogen ion concentration in solutions being investigated.

To determine the hydrogen ion concentrations in the standard acid itself at different concentrations S. Sorensen multiplied the analytical concentrations of this acid by the degree of its dissociation determined according to the electrical conductivity. A pH scale based on standards of hydrogen ion concentration calculated in this way is often used for practical purposes at present.

However, pH values based on the analytical concentration of hydrogen ions cannot be used in accurate investigations, since the thermodynamic properties of solutions depend not on the analytical concentration, but on the activity of the ions in the solution. For this reason at present by the term pH is meant the logarithm of the activity of hydrogen ions taken with the reverse sign (the symbol $pH_a$ is used by some authors for this quantity instead of pH):

$$pH_a = -\log a_{H^+} \tag{18.64}$$

For dilute solutions the values of the concentration and the activity coincide. For concentrated solutions the values of pH calculated according to the analytical concentration and according to the activity of the hydrogen ions may diverge considerably.

In an aqueous medium a hydrogen ion, as was indicated previously, combines with a molecule of water, forming a hydroxonium ion

$H_3O^+$. In pure water $[H_3O^+] = [OH^-]$. At 25 °C we have $k_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$, consequently $[H_3O^+] = 10^{-7}$ and pH = 7.

In principle we could also use the hydroxyl ion concentration pOH. For pure water pOH is obviously also equal to 7. But at a constant temperature pH + pOH = const, therefore to characterize both the acid and the basic properties of aqueous solutions it is quite sufficient to know only the pH.

In acidic solutions $[H^+] > 10^{-7}$ and, consequently, pH < 7. In alkaline solutions, on the contrary, $[H^+] < 10^{-7}$ and the pH is correspondingly greater than 7.

In principle the concentrations of other ions or molecules could also be expressed by using the corresponding ion concentrations, for example $pNa^+$, $pSO_4^{2-}$, and $pCH_3OH$. But in practice only the pH, characterizing the acidity of a medium, has found broad application.

The pH is rarely negative in practice. Thus, if $[H^+] = 1$, then pH = 0, and only at $[H^+] = 10$ does the pH reach the value of minus one. The hydrogen ion concentration corresponding to pH = —1 is very great and is rarely encountered, and a concentration corresponding to pH = —2 is simply impossible.

For more accurate calculations of the pH in concentrated solutions and for taking account of the influence of the ionic strength on the activity of a solution see Sec. 22.6. Using the methods set out there, we can compute the true values of the ionic product of water, the thermodynamic dissociation constants for acids and bases and other characteristics of ionic equilibria in concentrated solutions.

As mentioned above, the pH is frequently determined with the aid of e.m.f. measurements. Such measurements give not the concentration, but the activity of hydrogen ions. The accuracy and convenience of the e.m.f. method appreciably facilitated the fact that at present it is accepted practice to determine $pH_a = -\log a_{H^+}$.

In determining the hydrogen ion concentration in solutions in usual laboratory practice, however, the activity coefficients are frequently neglected and $pH = -\log [H_3O^+]$ is determined, i.e. formulas containing the analytical concentrations are used. This reduces accuracy, but simplifies the calculations.

**18.11. Indicators.** *Indicators* are substances that are capable of changing their colour depending on the activity or concentration of the hydrogen ions in a solution. Many indicators are used in the titration of acids with alkalies or vice versa, but very few indicators change their colour near the point of neutralization, i.e. when the pH of the solution only slightly differs from 7. The change in colour (see Table 18.6) occurs within the interval of 1.5-2 units of the pH and may take place either in acid or in alkaline solutions, depending on the nature of the indicator. This diversity in the values of the pH at which different indicators change their colour is used to measure the pH.

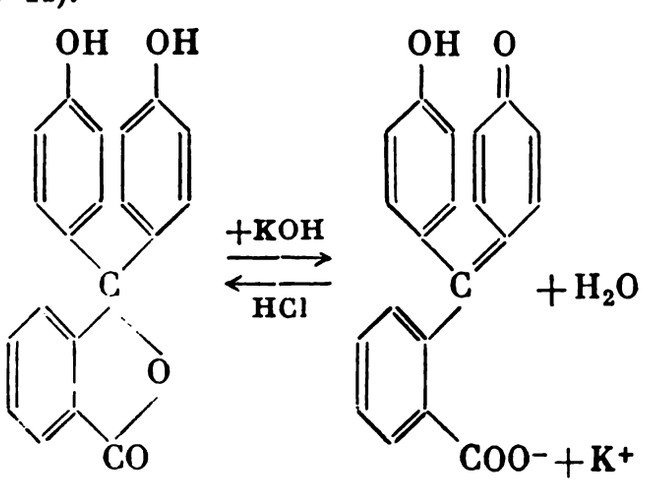
TABLE 18.6

**Selected Indicators and Their Characteristic Properties**

| Indicator | $pk_{in}$[1] | Interval of colour change, pH | Colour | |
|---|---|---|---|---|
| | | | in acid | in alkali |
| Thymol blue | 1.51 | 1.2-2.8 | red | yellow |
| Methyl orange | 3.7 | 3.1-4.4 | red | yellow |
| Bromphenol blue | 3.98 | 3.0-4.6 | yellow | blue |
| Bromcresol green | 4.67 | 3.8-5.4 | yellow | blue |
| Bromcresol red | 5.1 | 4.2-6.3 | red | yellow |
| Chlorophenol red | 5.98 | 4.8-6.4 | yellow | red |
| Bromphenol | 6.16 | 5.2-6.8 | yellow | red |
| Bromcresol purple | 6.3 | 5.2-6.8 | yellow | purple |
| Bromthymol blue | 7.0 | 6.0-7.6 | yellow | blue |
| *n*-Nitrophenol | 7.1 | 5.6-7.6 | colourless | yellow |
| Phenol red | 7.9 | 6.8-8.4 | yellow | red |
| Cresol red | 8.3 | 7.2-8.8 | yellow | red |
| Metacresol purple | 8.32 | 7.4-9.9 | yellow | purple |
| Thymol blue | 8.9 | 8.0-9.6 | yellow | blue |
| Cresolphthalein | 9.4 | 8.2-9.8 | colourless | red |
| Phenolphthalein | 9.4 | 8.3-10.0 | colourless | red |
| Thymolphthalein | 9.4 | 9.2-11.6 | colourless | blue |
| Alizarin yellow | — | 10.0-12.0 | yellow | lilac |
| Nitroamine | — | 11.0-13.0 | colourless | orange-brown |

[1] $pk_{in}$ similar to pH denotes log $k_{in}$

The theory of indicators was worked out by W. Ostwald (1891), A. Hantzsh (1907), N. Bjerrum (1918) and others. These authors found that indicators can exist in two tautomeric forms having a different colour. For example, phenolphthalein in an acid medium becomes colourless (form I), and in an alkaline medium reddish-violet (form II):




I II

In a general form the relations between the activities of the different forms of an indicator and the hydrogen ions can be written as follows. Let us denote by HB the undissociated acid form of the indicator, and by B the basic form. If the acid HB is a neutral molecule, its conjugate base B carries a negative charge. If the base B is neutral, the acid carries a positive charge. In addition, both the acid and the base can exist in a colourless (I) or coloured (II) tautomeric form, namely $HB_I$ and $HB_{II}$ and correspondingly $B_I$ and $B_{II}$.

Let us consider the case when the acid is without a charge. When it interacts with water we have

$$HB_I + H_2O = B_I^- + H_3O^+$$

The dissociation constant of this reaction

$$K_{d_I} = \frac{a_{H_3O^+} a_{B_I^-}}{a_{HB_I}} \tag{18.65}$$

The colourless ion $B_I^-$ is in tautomeric equilibrium with the coloured form $B_{II}^-$

$$B_I^- \rightleftarrows B_{II}^-$$

The constant of this equilibrium

$$K_{a_B} = \frac{a_{B_{II}^-}}{a_{B_I^-}} \tag{18.66}$$

The coloured ions $B_{II}^-$ formed should also be in equilibrium with the hydrogen ions, since the following reaction is possible:

$$HB_{II} + H_2O = B_{II}^- + H_3O^+$$

and, consequently, the dissociation constant for the acid $HB_{II}$ is

$$K_{d_{II}} = \frac{a_{B_{II}^-} a_{H_3O^+}}{a_{HB_{II}}} \tag{18.67}$$

In addition to the independent equilibria listed above, another equilibrium can be written between the total amounts of undissociated and dissociated acid regardless of the form in which these amounts are present:

$$[HB_I + HB_{II}] + H_2O = [B_I^- + B_{II}^-] + H_3O^+$$

The summary dissociation constant of the indicator is

$$K_{d_{in}} = \frac{(a_{B_I^-} + a_{B_{II}^-})\, a_{H_3O^+}}{a_{HB_I} + a_{HB_{II}}} \tag{18.68}$$

The quantity $K_{d_{in}}$ can be expressed through $K_{d_I}$, $K_{d_{II}}$ and $K_{a_B}$. For this purpose the values of $a_{HB_I}$ and $a_{HB_{II}}$ found from Eqs. (18.65) and (18.67) should be inserted into Eq. (18.68) and the numerator and denominator of the right-hand part divided by $a_{B_I^-}$. The result is

$$K_{d_{in}} = \frac{K_{d_I} K_{d_{II}} (1 + K_{a_B})}{K_{d_{II}} + K_{d_I} K_{a_B}} \tag{18.69}$$

From Eq. (18.68) we obtain

$$a_{H_3O^+} = K_{d_{in}} \frac{a_{HB_I} + a_{HB_{II}}}{a_{B_I^-} + a_{B_{II}^-}}$$

If the ionic strength is low, the activities may be replaced by the concentrations

$$[H_3O^+]=k_{in}\frac{[HB_I]+[HB_{II}]}{[B_I^-]+[B_{II}^-]} \tag{18.70}$$

where $k_{in}$ is the so-called *indicator constant.*

For a substance to serve as a good indicator, form I must predominate in the undissociated state, and form II in the dissociated one, or vice versa. Assume that $[B_{II}^-] \gg [B_I^-]$. This means that the approximate tautomeric constant

$$k_B=\frac{[B_{II}^-]}{[B_I^-]}$$

is sufficiently great. According to the set condition, $[HB_I]$ must be much greater than $[HB_{II}]$. To find out when this is possible, let us divide Eq. (18.67) by Eq. (18.65), replacing the activities with the concentrations and the dissociation constants with the dissociation functions. We obtain

$$\frac{k_{II}}{k_I}=\frac{[H_3O^+][B_{II}^-][HB_I]}{[HB_{II}][H_3O^+][B_I^-]}=k_B\frac{[HB_I]}{[HB_{II}]}$$

The ratio $[HB_I]/[HB_{II}]$ may be sufficiently great if $k_{II}/k_I$ is considerably greater than $k_B$ which, as already noted above, must itself be sufficiently great. This means that the tautomeric form $HB_{II}$ must be a much stronger acid than the form $HB_I$.

In the same way we find that with a stronger acid $HB_I$ the base $B_I^-$ should predominate in the dissociated state. Thus, if the coloured form is a stronger acid, it is almost completely dissociated; as acid is added to the solution, dissociation is suppressed, but in the undissociated acid equilibrium is appreciably displaced in the direction of the colourless form $HB_I$, since this acid is weaker. Therefore, for a good indicator the ratio of the amount of dissociated molecules to that of undissociated ones is practically equal to the ratio of the concentrations of two differently coloured forms, and hence, according to Eq. (18.70)

$$a_{H_3O^+}\approx[H_3O^+]=k_{in}\frac{\text{Concentration of undissociated indicator}}{\text{Concentration of dissociated indicator}}$$

or

$$a_{H_3O^+}\approx[H_3O^+]=k_{in}\frac{1-\alpha}{\alpha} \tag{18.71}$$

Equation (18.71) shows that the relation between the concentrations of the dissociated and undissociated parts of the indicator, and consequently the colour of the solution, depend on the activity or correspondingly the concentration of the hydrogen ions in the solution.

Not all indicators are acids in the undissolved state. If the indicator introduced into the solution is a base, its reaction with water results in the formation of the conjugate acid, and all the calculations given above are applicable to the system obtained.

It has been established experimentally that the colour of the undissociated form begins to change appreciably when about 9% of the indicator has transformed into the dissociated form, i.e. when $\alpha = 0.09$. According to Eq. (18.71) we have

$$[H_3O^+]=k_{in}\frac{0.91}{0.09};\quad \log[H_3O^+]=\log k_{in}+\log\frac{0.91}{0.09};\quad -pH=-pk_{in}+1$$

$$\text{and}\quad pH=pk_{in}-1 \tag{18.72}$$

where $pk_{in}$, similar to pH, denotes $-\log k_{in}$.

Correspondingly, the eye stops noting an admixture of the colour of the initial form when the degree of dissociation reaches 91%. Repeating the previous calculation for $\alpha = 0.91$, we get

$$pH = pk_{In} + 1 \tag{18.73}$$

When the indicator is half dissociated, we have

$$[H_3O^+] = k_{In}\frac{0.50}{0.50} \quad \text{and} \quad pH = pk_{In} \tag{18.74}$$

Equations (18.72), (18.73) and (18.74) show that a change in colour occurs within the limits of two units of the pH, namely from $pH = pk_{In} - 1$ to $pH = pk_{In} + 1$, and at the middle of this interval $pH = -\log k_{In}$. Figure 18.3 contains a curve showing the change in the intensity of the colour in the titration of an acid solution with an alkali in the presence of phenolphthalein. Points *a* and *b* correspond to moments when the eye begins to notice and stops noticing the change in the colour. The curve was obtained with the aid of a spectrophotometer, which is naturally much more sensitive than the human eye. The dissociation function of the indicator can be determined in different ways. For example:

1. If the indicator dissociates, but very weakly, then the equivalent conductivity of solutions of different concentrations can be used to find the corresponding degrees of dissociation $\alpha$ and compute the dissociation function.

2. If the indicator acquires a different colour in an acid and an alkaline medium, then two solutions can be prepared in two vessels with plane-parallel walls, the distances between which are the same. One of the solutions is so acid and the other so alkaline that the indicator in them does not acquire an intermediate colour. The concentration of the indicator in both solutions should be the same. Placing the coloured layers one above the other, we examine them in passing light and compare the colour observed with that of a number of solutions with a different pH. The thickness of the layer of these solutions should be the same as that of each of the two standard ones. Since this thickness is half of the total thickness of the acid and alkaline solutions, a double amount of the indicator must be added to the solution being compared. In a solution whose colour will coincide with that of the two-layer standard one, the indicator is half dissociated and, therefore, $pk_{In} = pH$ for this solution. In this way we can find only the dissociation function of the indicator, since it is based on the assumption that one coloured form is completely dissociated, and the other is completely undissociated.

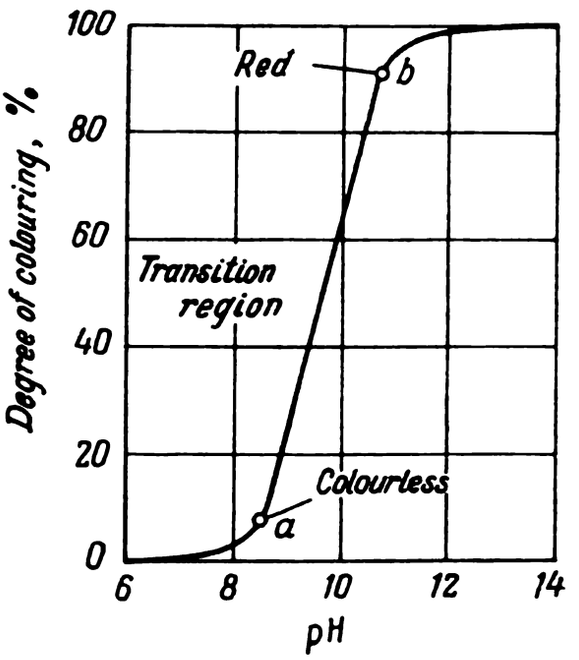



Fig. 18.3. Dependence of colour of phenolphthalein on pH of solution

**18.12. Buffer Solutions.** Solutions having a definite pH and capable of retaining it almost constant when a strong acid or a strong base is added to them are called *buffer solutions* or *buffers*. This ability, called *buffer action*, manifests itself depending on the composition of the solution. The magnitude of the buffer action, called the *buffer value* or *buffer index*, is measured by the amount of strong

acid or base that must be added to change the pH of the solution by unity.

Buffer solutions usually consist of a weak acid and its conjugate base, for example of acetic acid and a salt of this acid and a strong base. Such salts dissociate quite well and, consequently, the solution contains a conjugate pair

$$CH_3COOH \text{ and } CH_3COO^-$$

whose action consists in that with the addition of a strong acid the protons given up by the latter are bound by the base $CH_3COO^-$. When a strong base is introduced, the acetic acid gives up its protons to it. Thus in both cases the concentration of the hydrogen ions changes insignificantly.

The quantitative relation between the value of the pH and the activities or, for dilute solutions, the concentrations of the solutes is found from the expression for the dissociation function:

$$k_{CH_3COOH} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \tag{18.75}$$

Let us find the hydrogen ion concentration

$$[H_3O^+] = k_{CH_3COOH} \frac{[CH_3COOH]}{[CH_3COO^-]} \tag{18.76}$$

If to a solution of a weak acid we add a salt of this acid and a strong base that well dissociates into ions, the dissociation of the acid will be suppressed, and in the first approximation the concentration of the molecules of $CH_3COOH$ may be considered equal to that of all the acetic acid in the solution. On the other hand, since the salt $CH_3COONa$ is a strong electrolyte, the concentration of the ions $CH_3COO^-$ may be considered equal to that of all the dissolved salt.

TABLE 18.7

**Walpole's Buffer Mixtures of *M*/5 Acetic Acid and *M*/5 Sodium Acetate**

| pH | Concentration (molar) | | pH | Concentration (molar) | |
|---|---|---|---|---|---|
| | acetic acid | sodium acetate | | acetic acid | sodium acetate |
| 3.6 | 0.185 | 0.015 | 4.8 | 0.080 | 0.120 |
| 3.8 | 0.176 | 0.024 | 5.0 | 0.059 | 0.141 |
| 4.0 | 0.164 | 0.036 | 5.2 | 0.042 | 0.158 |
| 4.2 | 0.147 | 0.053 | 5.4 | 0.029 | 0.171 |
| 4.4 | 0.126 | 0.074 | 5.6 | 0.019 | 0.181 |
| 4.6 | 0.102 | 0.098 | | | |

On the basis of what has been said above we get

$$[H_3O^+] = k_{CH_3COOH} \frac{[CH_3COOH]}{[CH_3COONa]} \quad (18.77)$$

or

$$pH = -\log k_{CH_3COOH} - \log[CH_3COOH] + \log[CH_3COONa] \quad (18.78)$$

Thus, by selecting different concentrations or, more exactly, different ratios of the acid and salt concentrations, we can obtain solutions with different values of the pH (Table 18.7).

At a given composition of a solution the pH only slightly depends on the temperature, since the value of the dissociation function does not practically change with the temperature.

Let us consider quantitatively with the buffer solution of $CH_3COOH + CH_3COONa$ taken as an example how the pH of the solution changes when a strong acid or strong base is added ($k_{CH_3COOH}$ at 25 °C is equal to $1.752 \times 10^{-5}$).

When a strong acid, for instance HCl, is added to this buffer solution, the following reaction proceeds:

$$CH_3COO^- + Na^+ + H_3O^+ + Cl^- = CH_3COOH + Na^+ + Cl^- + H_2O \quad (18.79)$$

As a result the denominator in the right-hand part of Eq. (18.77) decreases, while the numerator grows and the pH of the solution drops.

The ions $Na^+$ and $Cl^-$ affect the pH only so far as they change the ionic strength of the solution, which the activity coefficients depend on. In accurate calculations this influence must be taken into account.

When a strong base, for instance NaOH, is added, the following reaction proceeds:

$$CH_3COOH + Na^+ + OH^- = CH_3COO^- + Na^+ + H_2O \quad (18.80)$$

and the pH accordingly increases somewhat.

Let us assume that 1 $dm^3$ of the solution at 25 °C contains one mole of $CH_3COOH$ and one mole of $CH_3COONa$, which according to Eq. (18.78) corresponds to

$$pH = -\log k_{CH_3COOH} - \log 1 + \log 1 = -\log 1.752 \times 10^{-5} = 4.756$$

If we add 0.9 mole of HCl to the solution, as a result of reaction (18.79) the concentrations of $CH_3COO^-$ and $CH_3COOH$ change, and the pH decreases by 1.278, namely, $pH = 4.756 - \log 1.9 + \log 0.1 = 4.756 - 0.278 - 1 = 3.478$. If the solution were not a buffer one, then for the same change in the pH not 0.9 mole of HCl would be required, but only

$$10^{-3.478} - 10^{-4.756} = 0\,000\,32 - 0\,000\,017\,5 = 0.000\,30 \text{ mole of HCl}$$

Similar results (only with an increase in the pH) are obtained when a strong base is added to the solution.

Calculating the change in the pH of the same initial solution if only 0.1 mole of HCl is added to it, we get $pH = 4.756 - \log 1.1 + \log 0.9 = 4.668$, i.e. the pH changes by approximately 0.1.

Attention should be given to the fact that the change in the pH depends not on the absolute amount of strong acid (or strong base)

added, but on the ratio

$$\frac{\text{number of moles of HCl (or NaOH) added per unit of volume}}{\text{number of moles of initial } CH_3COONa \text{ (or } CH_3COOH\text{) per unit of volume}}$$

Thus the buffer properties of the solution continuously weaken as the $CH_3COONa$ is consumed if HCl is added, and as the $CH_3COOH$ is consumed if NaOH is added.

By the buffer value or index is meant the number of gramme-equivalents of a strong acid (or strong base) that must be added to a solution to change its pH by unity.

Let us consider a solution containing 0.8 g-eq of $CH_3COOH$ and 0.2 g-eq of $CH_3COONa$ in one cubic decimetre. The pH of such a solution according to Eq. (18.78) is equal to

$$pH = -\log k_{CH_3COOH} - \log[CH_3COOH] + \log[CH_3COONa]$$

$$pH = -\log 1.76 \times 10^{-5} - \log 0.8 + \log 0.2 = 4.152$$

When an amount of an acid corresponding to the buffer index of the solution is added to it, the pH should be brought up to the value 3.15. Here the value of $[CH_3COOH]$ grows, and that of $[CH_3COONa]$ decreases by the same amount. Let us denote the change in concentration by $x$ and write the equation

$$3.152 = -\log 1.76 \times 10^{-5} - \log (0.8 + x) + \log (0.2 - x)$$

Solution of this equation gives $x = 0.175$ g-eq/dm$^3$.

In determining the buffer index with respect to an alkali, we write a similar equation, taking into account that the pH should be brought up to the value 5.152, the value of $[CH_3COOH]$ decreases and that of $[CH_3COONa]$ grows by the same amount, namely,

$$5.152 = -\log 1.76 \times 10^{-5} - \log (0.8 - x) + \log (0.2 + x)$$

whence $x = 0.515$ g-eq/dm$^3$.

The buffer indices of the solution with respect to the acid and the alkali are different, since the concentrations $[CH_3COOH]$ and $[CH_3COONa]$ are not the same.

When a buffer solution is diluted with water, the ratio of the analytical concentrations of the weak acid and its salt remains constant. The activity coefficients may change differently, however. But in the dilution of buffer solutions their pH changes insignificantly, and this change may often be neglected. For example, the pH of a mixture of identical volumes of an $N/15$ solution of $Na_2HPO_4$ and an $N/15$ solution of $NaH_2PO_4$ is equal to 6.81. After a dilution of five times the pH is 6.99, after a dilution of 20 times it is 7.07, and of 100 times—7.10. This example also shows that buffer mixtures can be prepared not only using an acid (or a base) and a salt, but also using two salts at different degrees of dissociation. Such buffer systems as $H_2CO_3 + NaHCO_3$ and $Na_2HPO_4 + NaH_2PO_4$ are of

a great significance in the physiology of living organisms, since the constancy of the pH is essential for the proper functioning of various organs.

Buffer mixtures are widely used for the preparation of standard solutions with a given pH. They serve for determining the hydrogen ion concentration by comparing the colour of an indicator added to the standard solutions and to the colourless solutions being investigated. The pH of the standard mixtures is established by the e.m.f. method.

Table 18.8 gives selected buffer solutions used for the preparation of a series of solutions with different intervals of pH values. Within the limits of these values, the change in the colour of the indicator is entirely completed.

TABLE 18.8
**Buffer Solutions**

| Composition | pH range |
|---|---|
| Hydrochloric acid + calcium chloride | 1.0-2.2 |
| Glycine + hydrochloric acid | 1.0-3.7 |
| Potassium hydrogen phthalate + hydrochloric acid | 2.0-3.8 |
| Sodium phenylacetate + phenylacetic acid | 3.2-4.9 |
| Amber acid + borax | 3.0-5.8 |
| Acetic acid + sodium acetate | 3.7-5.6 |
| Potassium hydrogen phthalate + sodium hydroxide | 4.0-6.2 |
| Dibasic sodium citrate + sodium hydroxide | 5.0-6.3 |
| Monobasic potassium phosphate + sodium hydroxide | 5.8-8.0 |
| Boric acid + borax | 6.8-9.2 |
| Diethylmalonylurea acid + sodium salt of this acid | 7.0-9.2 |
| Borax + hydrochloric acid | 7.6-9.2 |
| Boric acid + sodium hydroxide | 7.8-10.0 |
| Glycine + hydrochloric acid | 8.2-10.1 |
| Borax + sodium hydroxide | 9.2-11.0 |
| Dibasic sodium phosphate + sodium hydroxide | 11.0-12.0 |

**18.13. Measurement of Activity (Concentration) of Hydrogen Ions.** The activity of hydrogen ions, which in dilute solutions may be taken equal to the concentration, is determined the most accurately by the e.m.f. method. This method is very precise and, in addition, it can be used for coloured and even completely opaque solutions. It should also be noted that any method used to determine the hydrogen ion concentration must meet the requirement of there being no change in the composition of a solution, since the introduction of any reagent changes the pH of the solution in some way. The use of indicators and the e.m.f. method meet this requirement to a sufficient degree, since here the influence of the introduced reagents on the pH may be neglected owing to their addition in the minutest amounts.

When a high accuracy is not required, the colorimetric method is used. It consists in preparing several series of standard buffer solutions. The solutions of each series differ from one another, for example, by 0.2 unit of the pH. Each series of solutions is coloured with an indicator and so selected that an interval of pH values is covered at which the colour of the indicator changes. The indicators are so selected according to Table 18.6 that the intervals of the pH values at which the colour of each indicator changes partly overlap, filling the entire scale of the pH values being measured. Commercial sets of prepared standard solutions already coloured with an indicator usually cover a scale of pH values from 1 to 12.

Such a set can be used to rapidly measure the pH of an unknown but colourless solution. Measurement of the pH consists in comparing the colour of the solution being investigated, which an indicator is added to, with the colour of the standard solutions. Although the colorimetric method is less accurate than the electrometric one (the smallest error of the colorimetric method is 0.02-0.05 pH unit), the great simplicity of the apparatus and the rapidity of measurements have brought it into great favour.

When selecting indicators attention should be given not only to suitable intervals of colour change, but also to the fact that the indicator should give a stable colour and have the lowest possible sensitivity to a change in the ionic strength of the solution (salt error) and to a change in the content of proteins and other colloids (protein error).

The most complete series of indicators proposed by S. Sorensen for work with buffer solutions contains 18 indicators and covers a pH range from 0.1 to 12.7. Frequently a smaller set of indicators is quite sufficient for determining the pH (Table 18.9).

TABLE 18.9

**Sets of Indicators for Determining the pH**

| Indicator | Colour change | pH range |
|---|---|---|
| | *Set of Clark and Lubs* | |
| Thymol blue | Red-yellow | 1.2-2.8 |
| Bromphenol blue | Yellow-blue | 3.0-4.6 |
| Methyl red | Red-yellow | 4.4-6.0 |
| Bromcresol purple | Yellow-purple | 5.2-6.8 |
| Bromthymol blue | Yellow-blue | 6.0-7.6 |
| Phenol red | Yellow-red | 6.8-8.4 |
| Cresol red | Yellow-red | 7.2-8.8 |
| Thymol blue | Yellow-blue | 8.0-9.6 |
| Cresolphthalein | Colourless-red | 8.2-9.8 |
| | *Set of Michaelis* | |
| β-Dinitrophenol | Colourless-yellow | 1.7-4.4 |
| α-Dinitrophenol | Colourless-yellow | 2.0-4.7 |
| γ-Dinitrophenol | Colourless-yellow | 4.0-6.0 |
| *p*-Nitrophenol | Colourless-yellow | 5.0-7.0 |
| *m*-Nitrophenol | Colourless-yellow | 6.5-8.5 |
| Phenolphthalein | Colourless-red | 8.3-10.5 |
| Alizarin yellow | Colourless-yellow | 10.0-12.0 |

The set of indicators proposed by Clark and Lubs consists of nine indicators and covers a range of pH values from 1.2 to 9.8. L. Michaelis proposed a different method of using indicators and the corresponding series of them. A glance at Table 18.9 shows that all the indicators of the Michaelis series give a change from a colourless form to a coloured one. This makes it possible to determine the value of the pH within the interval of the change of one form to the other not according to the tint of the colour, as with the Clark and Lubs indicators, but according to the intensity of a definite colour. Owing to this feature, the series of indicators selected by Michaelis makes it possible to measure the pH without preparing series of buffer solutions. The Michaelis method is based on the fact that all the indicators of the series are weak acids giving the colourless form in the undissociated state and the coloured one in a dissociated state. The changes in colour occur within the ranges of pH indicated in Table 18.9.

If we take a sufficiently concentrated solution of an alkali, the indicator added to it will be completely dissociated, and, therefore, the number of indicator ions in the solution is determined by the amount of indicator added. Using this relation, Michaelis added different amounts of an indicator to a series of test tubes containing a concentrated solution of an alkali. Thus a series of solutions were obtained with a different colour intensity, the latter depending only on the amount of indicator added. Then the test tube was selected in which the intensity of the colour of the solution coincided with that of the solution being investigated containing the same indicator.

Coincidence of the colour intensity indicates that the concentration of the indicator ions in both solutions is the same. The value of the indicator concentration in the standard test tube is known, since an accurately measured amount of the indicator was added to the alkaline solution. Thus, knowing the concentration of the indicator added to the solution being investigated and the concentration of the indicator ions by comparison with the standard solutions, we can calculate the degree of dissociation of the indicator in the solution being investigated. Knowing the dissociation constants of the indicators of the Michaelis series, we can compute the hydrogen ion concentration, i.e. the pH of the solution being investigated by Eq. (18.71).

The Michaelis method is very simple, and for this reason it is in great favour, although the Michaelis series covers a smaller pH range than the series of buffer solutions considered earlier.

The pH is measured very accurately with the aid of a spectrophotometer. This instrument makes it possible to appraise the intensity of spectrum lines. First the intensity of the spectrum lines of both forms of an indicator is measured. The next step is to photograph the spectrum of a solution coloured by the same indicator. Then by comparing this spectrum with those for both forms of the indicator, the ratio between the concentrations of the two forms in the solution being investigated is found. This ratio allows us to compute the pH.

TABLE 18.10

**Change in Colour of Universal Indicator Depending on pH of Solution**

| pH | Colour | pH | Colour |
|---|---|---|---|
| 4 | Red | 8 | Green |
| 5 | Orange-red | 9 | Bluish-green |
| 6 | Yellow | 10 | Bluish-violet |
| 7 | Yellow-green | 11 | Red-violet |

Preliminary or approximate measurements can be performed with great convenience with the aid of a universal indicator. This is a mixture of several indicators so selected that the colour of the solution changes continuously upon a gradual change from pH = 3 to pH = 11. An example of the change in colour of a convenient and simple mixture serving as a universal indicator is given in Table 18.10.

The mixture is composed of equal volumes of 0.1 *N* solutions of methyl red, α-naphtholphthalein, thymolphthalein, phenolphthalein and bromthymol blue.

The pH is determined in non-aqueous solutions in the same way as in aqueous ones. In this case too the e.m.f. method is the most accurate one (see Sec. 22.6).

**18.14*. Comparison of Acidity of Solutions in Various Solvents.** In dealing with certain problems of both a theoretical and experimental nature, it becomes necessary to compare the acidity of solutions in various solvents. A way of solving this problem that is correct in principle was laid out by J. Brönsted. He proposed to compare the activity of a proton in the medium in question with its absolute activity, which it should have if the acid being considered were in a vacuum. Brönsted selected this state of the acid as a standard one. The dissociation constant of an acid expressed through the activities related to a state of the dissociation products in a vacuum is called the *absolute constant* and is designated by

$$K_A = \frac{a_{H^+} a_B}{a_A}$$

where $a_{H^+}$, $a_B$ and $a_A$ are the *absolute activities of a proton and of a conjugate acid and base.*

To determine the values of $a_A$ and $a_B$ it is necessary to know the values of $a_A^*$ and $a_B^*$. The latter are the activities of the acid and base in a given solvent related to their activities in the same solvent at an infinitely low concentration, when the activity coefficients are taken equal to unity. The values of $a_A^*$ and $a_B^*$ are usually found experimentally. In addition, it is necessary to find the values of $\gamma_{0,A}$ and $\gamma_{0,B}$, the *absolute activity coefficients.* These coefficients express the ratio of the activity of an acid or base in a solution at infinite dilution to their activity in a vacuum, also at an infinitely small concentration, when the activity coefficients $\gamma_{0,A}$ and $\gamma_{0,B}$ are taken equal to unity. The absolute activities of an acid and a base are equal to

$$a_A = a_A^* \gamma_{0,A} \quad \text{and} \quad a_B = a_B^* \gamma_{0,B}$$

Knowing $K_A$, $\gamma_{0,A}$ and $\gamma_{0,B}$ for a solution of an acid, we can calculate the absolute value $a_{H^+}$ for this acid and, by comparing the activities of the acid in various solvents with the found value of $a_{H^+}$, we can compare the acidities of the solutions being studied. The main difficulty here lies in the determination of the absolute activity coefficients. They can be calculated if we know the energy of transfer of the acid and base from a vacuum into the given solvent, i.e., the solvation energy.

The absolute acidity constant $K_A$ can be calculated on the basis of values of the proton affinity, i.e. the work of attaching a proton to the acid and base in a vacuum. At present, however, the accuracy of determining the proton affinity is still insufficient. Thus the problem of comparing the acidity of solutions in various solvents will be solved when sufficiently accurate methods are discovered for determining the absolute activity coefficients and the proton affinity.

Since a thermodynamically faultless method of calculation is not available at present, L. Hammett proposed to appraise the acidity of any solutions, i.e. their pH, according to the degree of transformation of an indicator-base to its

ionic form. This method is based on experimental data, according to which the dissociation functions of bases (cationic acids) are approximately the same in different solvents. If a base is the indicator, then according to Eq. (18.71) we get the relation

$$pH = -\log k_{In} + \log \frac{[B]}{[BH]}$$

where [B] and [BH] are the concentrations of the indicator-base and its ion. The concentrations of the acid and basic forms of the indicator are determined by colorimetric procedures. The colour of the solution being investigated is compared with that of another solution in which the indicator is entirely in one of the coloured forms. Indicators having one colourless and one coloured forms are especially convenient here.

Hammett's method is exceedingly simple. For this reason it has found very broad application, notwithstanding its comparatively low accuracy. It should be taken into account that on one hand the dissociation functions for bases nevertheless depend somewhat on the nature of the solvent. On the other hand the indicator method has a number of limitations, namely, the colour of the indicator and its intensity depend not only on the pH of a solution, but also on the presence of oxidizers or reducers, on the ionic strength of the solution, and on the presence of proteins in the solution (protein error). The introduction of the indicator itself affects the pH. At large intervals of the pH several indicators have to be used, which introduces complications into the results of measurements, and, in addition, a series of indicators selected for one solvent will not be equivalent in another one.

**18.15. Titration Curves.** In the titration of acids with bases or bases with acids different values of the pH correspond to the same amount of the equivalent acid and base in the solution. These values depend on the strength of the acid and base reacting in titration. Curves showing the dependence of the pH of the acid (or base) solution being titrated on the amount (usually the volume of the solution in $cm^3$) of base (or respectively acid) added are called *titration curves*. A point on a titration curve corresponding to identical amounts of acid and base equivalents in the solution is called an *equivalent point*. If the reaching of the equivalent point is to be determined with the use of an indicator, such an indicator should be taken that changes its colour at a pH corresponding to the equivalent point. Let us consider several examples.

1. A strong acid is titrated with a strong base. Assume that we have taken 10 $cm^3$ of a 0.1 $N$ solution of a strong acid, for instance HCl. The solution is titrated with a 0.1 $N$ solution of a strong base, for example KOH. The volume of the reaction mixture during titration continuously grows, which naturally affects the concentrations. In our further calculations, however, we shall neglect these changes in volume, which considerably simplifies calculations and does not practically influence the results.

Let us watch the change in the pH during titration. The pH for a 0.1 $N$ solution of a strong acid is equal to unity. After the addition of 9 $cm^3$ of the base solution, the concentration of the acid decreases 10 times and becomes equal to 0.01 $N$, which pH = 2 corresponds to.

To again reduce the concentration of the acid 10 times, it is necessary to add only 0.9 $cm^3$ of the base, after which pH = 3. Repeating the same calculations, we see that after the addition of another 0.09 $cm^3$ of the base solution the pH becomes equal to four, after the addition of another 0.009 $cm^3$ it becomes equal to five, and so on[1] until the equivalent point is reached (10 $cm^3$ of the base solution have been added). Now the system consists of water and a well dissociated salt, which corresponds to pH = 7. A curve showing this relation is depicted in Fig. 18.4.

When more base is added, the solution acquires an alkaline reaction, and the pH continues to grow. Initially a very small amount

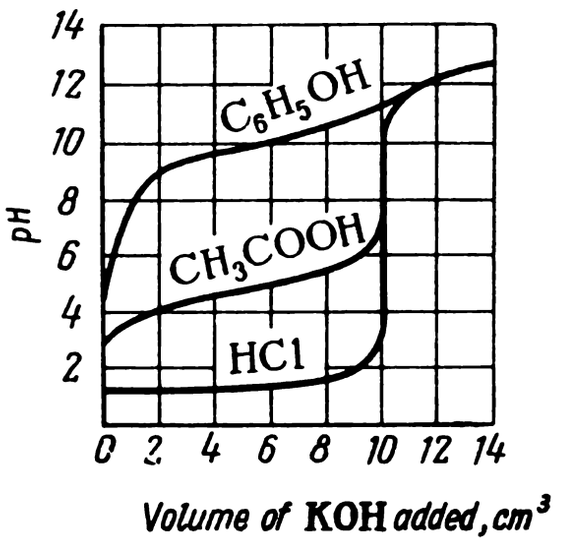



Fig. 18.4. Titration curves for acids

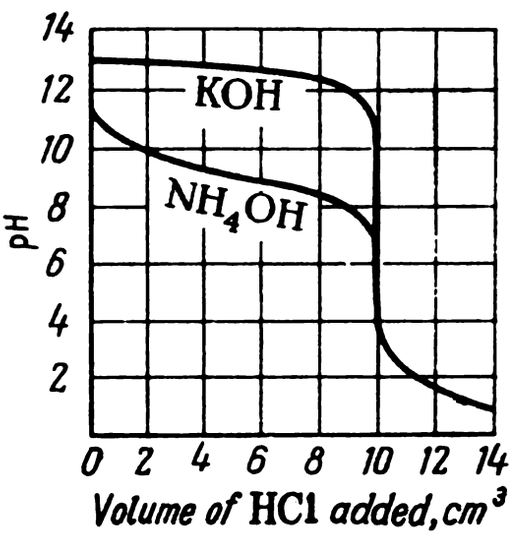



Fig. 18.5. Titration curves for bases

of the base is required for increasing the pH by unity, and the titration curve continues to rise practically vertically. Further its slope gradually decreases, and we get the upper branch of the titration curve shown in Fig. 18.4.

If a base is titrated with an acid, a dropping curve is obtained, which is absolutely symmetrical to the curve in Fig. 18.4 (see Fig. 18.5). The change in the pH of an acid solution as a base is added to it is shown in Table 18.11.

Since in the titration of a strong acid with a strong base the titration curve rises practically vertically in the pH range from about 3 to 11, titration can be conducted with any indicator that changes its colour within this range.

If the acid and the base are more diluted, for example to 0.001 $N$, the titration curve is within narrower limits of the pH, namely, it begins at pH = 3 and terminates at pH = 11. The vertical part

[1] Near the equivalent point this elementary calculation becomes somewhat more complicated, since the dissociation of water cannot be neglected.

TABLE 18.11
**Change in pH in Titration of 10 cm³ of a 0.1 *N* Solution of a Strong Acid with a 0.1 *N* Solution of a Strong Base**

| Amount of solution added, cm³ | $c_{H^+}$ | pH |
|---|---|---|
| — | $10^{-1}$ | 1 |
| 9.00 | $10^{-2}$ | 2 |
| 9.90 | $10^{-3}$ | 3 |
| 9.99 | $10^{-4}$ | 4 |
| 10.00 | $10^{-7}$ | 7 |
| 10.01 | $10^{-10}$ | 10 |

of the curve is approximately within the pH values from only 5 to 9. The more dilute the solutions of the acid and base taken, the less clear is the vertical section of the curve. At initial concentrations of 0.0001 *N* this part of the curve is within the pH values from 6 to 8, i.e. it is practically absent. In the titration of a strong acid with a strong base or vice versa, the calculation of the pH of the solution for any titration stage is sufficiently simple on condition that the activity coefficient may be neglected. It is not difficult to introduce a correction for the change in the volume of the solution in titration.

2. In the titration of a weak acid, for instance $CH_3COOH$, with a strong base, for instance KOH, the pH of the solution changes in a different way. Already in the initial 0.1 *N* solution of the acid the pH is 3. Upon the addition of the strong base the well dissociating salt $CH_3COOK$ and water are formed. The free $CH_3COO^-$ ions suppress dissociation of the acid. In addition part of the salt is hydrolyzed; the $OH^-$ ions formed also reduce the concentration of the $H^+$ ions. All this leads to a more rapid growth of the pH in the reaction medium. This is shown by the beginning of the curve for $CH_3COOH$ in Fig. 18.4. When the concentrations of the remaining free acid and the salt formed become approximately identical, a buffer mixture is obtained whose pH changes very slowly as the base is added. The addition of KOH from 2 to 8 cm³ corresponds to this slow rise of the curve in Fig. 18.4. After the buffer value of the solution is exhausted, the further addition of the base solution again leads to a more rapid growth of the pH. A state close to the equivalent one is reached not at pH = 3, as in the preceding example, but at pH > 7, since the potassium acetate formed is partly hydrolyzed. With the further addition of KOH to a solution consisting of water and the well dissociating salt $CH_3COOK$, the pH changes in practically the same way as in the titration of a strong acid with a strong base after the equivalent point has been passed. As can

be seen from Fig. 18.4, here it is necessary to use an indicator that changes its colour within pH values ranging from 8 to 10, for example phenolphthalein, whose colour change corresponds to a pH from 8.3 to 10 (see Table 18.6).

The accuracy with which the content of an acid in a solution can be determined by titration depends on the conditions which the acid is in. If another acid or several acids are present in the solution, the base added will be distributed among all the acids depending on their dissociation constants. Thus, it is possible to accurately titrate any single acid only on condition that the amount of base bound by the other acids is smaller than the amount that we may neglect with the given accuracy of analysis.

In the titration of an aqueous solution of a weak acid we in essence have to deal with a mixture of two acids, since water can also be considered as a weak acid whose dissociation function is equal to

$$k_{H_2O} = \frac{[H_3O^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.5} = \frac{10^{-14}}{10^{1.7}} = 10^{-15.7}$$

Assume that a solution contains two acids, $HA_I$ and $HA_{II}$, the second acid is stronger, and the number of equivalents of the two acids is the same. The dissociation functions of the two acids will be

$$k_I = \frac{[H_3O^+][A_I^-]}{[HA_I]} \quad \text{and} \quad k_{II} = \frac{[H_3O^+][A_{II}^-]}{[HA_{II}]}$$

Division of the second equation by the first one yields

$$\frac{k_{II}}{k_I} = \frac{[A_{II}^-][HA_I]}{[A_I^-][HA_{II}]} \tag{18.81}$$

Since both acids are weak and titration is performed with a strong base, we may consider that the salts obtained are completely dissociated. For this reason the sum of the concentrations $[A_I^-] + [A_{II}^-]$ is equal to the concentration of all the base introduced into the solution by the given moment.

Equation (18.81) shows that when the initial concentrations of both acids are equal, i.e. $[HA_I] = [HA_{II}]$, the stronger acid binds a greater fraction of the base. If the initial concentrations are not equal, the distribution of the base also depends on the ratio of the concentrations.

If the second constant is many times greater than the first one, the base is almost completely bound only by the second acid, which makes it possible to perform separate titration of two acids. The accuracy of such titration is calculated with the aid of Eq. (18.81).

Assume that the dissociation function of the weak acid $k_{II} = 10^{-6}$. For water $k_I = 10^{-15.7}$. Suppose we have a 0.1 $N$ solution of an acid whose concentration is to be found with an accuracy up to

0.1% This means that when the concentration of the untitrated acid $[HA_{II}] = 10^{-4}$, the greater part of the base should still be bound by the acid, and not by the water. Since a very small part of the acid is untitrated, we can assume that the amount of the base used for titration of $[A_{II}^-] = 0.1$, and the water can be considered as practically unused, i.e. $[HA_I] = 55.5 = 10^{1.7}$. Inserting all the values listed above in Eq. (18.81), we get

$$\frac{10^{-6}}{10^{-15.7}} = \frac{0.1 \times 10^{1.7}}{0.0001[A_I^-]}$$

i.e. $[A_I^-] = 10^{-5}$. This indicates that the concentration of the still unbound acid $[HA_{II}]$, which is equal to $10^{-4}$, is ten times greater than the concentration $[A_I^-]$ of the already bound water, i.e. by the end of titration of the acid we can still neglect the consumption of the base reacting with the water. Thus an acid with a dissociation function of $k_{II} = 10^{-6}$ can be titrated in an aqueous solution with an accuracy up to 0.1% with an initial 0.1 *N* solution.

Inserting into Eq. (18.81) other initial data, we find that the accuracy of titration of an acid is the lower, the smaller are its concentration and its dissociation function. For example, the accuracy of titration of a 0.1 *N* solution of an acid having a dissociation function equal to $10^{-8}$ is lower than 1%. In more accurate calculations the activity coefficients should be taken into account.

The pH of a solution at different stages of titration of a weak acid with a strong base can be calculated with the aid of a rather complicated formula deduced below. Let us denote the initial molarity of a weak monobasic acid by $a$. If the acid is partly neutralized by the addition of $b$ equivalents per cubic decimetre of a strong base, the total amount of the equivalents of the acid HA and ions $A^-$ is equal to $a$:

$$a = c_{HA} + c_{A^-} \tag{18.82}$$

where $c_{HA}$ and $c_{A^-}$ are the concentrations, g-eq/dm³.

In addition to the ions $A^-$ and molecules HA, the solution contains the ions $OH^-$, $H_3O^+$ and ions of the metal of the base $Me^+$. The concentration of the latter is $b$. Since the solution should be electrically neutral, the sum of all the positive charges should be equal to that of all the negative charges, i.e.

$$c_{Me^+} + c_{H_3O^+} = c_{A^-} + c_{OH^-} \tag{18.83}$$

or

$$b + c_{H_3O^+} = c_{A^-} + c_{OH^-}$$

The dissociation constant for the acid $K_d$ can be expressed as follows:

$$K_d = \frac{a_{H_3O^+} a_{A^-}}{a_{HA}} = a_{H_3O^+} \frac{c_{A^-}}{c_{HA}} \frac{f_{A^-}}{f_{HA}} \tag{18.84}$$

where $f_{A^-}$ and $f_{HA}$ are the activity coefficients.

After transformation we get

$$a_{H_3O^+} = K_d \frac{c_{HA}}{c_{A^-}} \frac{f_{HA}}{f_{A^-}} \tag{18.85}$$

If we delete $c_{HA}$ and $c_{A^-}$ from Eq. (18.85), using Eqs. (18.82) and (18.83), then

$$c_{A^-}=b+c_{H_3O^+}-c_{OH^-}$$

$$c_{HA}=a-c_{A^-}=a-b-c_{H_3O^+}+c_{OH^-}$$

whence

$$a_{H_3O^+}=K_d\frac{a-b-c_{H_3O^+}+c_{OH^-}}{b+c_{H_3O^+}-c_{OH^-}}\frac{f_{HA}}{f_{A^-}} \tag{18.86}$$

To simplify the appearance of Eq. (18.86) let us denote the expression $b + c_{H_3O^+} - c_{OH^-}$ by $E$; then this equation becomes

$$a_{H_3O^+}=K_d\frac{a-E}{E}\frac{f_{HA}}{f_{A^-}} \tag{18.87}$$

or

$$pH_a=pK_d+\log\frac{E}{a-E}+\log\frac{f_{A^-}}{f_{HA}}$$

The last term in the right-hand part of Eq. (18.87) can be calculated with the aid of the Debye-Hückel equation (16.7), for example

$$\log f_{A^-}=-\frac{A\sqrt{I}}{1+Ba\sqrt{I}}+CI$$

where $I$ = ionic strength of the solution
$A$, $B$ and $C$ = constants.

The calculation of the $pH_a$ value by the full equation (18.87) is quite complicated, since after introducing $c_{OH^-}=\frac{K_w}{c_{H_3O^+}}$ we get a cubic equation with respect to $c_{H_3O^+}$. For this reason Eq. (18.87) is simplified by discarding all quantities that may be neglected.

If the ionic strength of a solution is sufficiently low and the activity coefficients can be taken equal to unity, which is approximately true for weak acids, the last factor in Eq. (18.86) may be discarded and the equation becomes

$$c_{H_3O^+}=K_d\frac{a-b-c_{H_3O^+}+c_{OH^-}}{b+c_{H_3O^+}-c_{OH^-}} \tag{18.88}$$

The possibility of further simplifications is determined by the different values of $c_{H_3O^+}$ and $c_{OH^-}$ at the beginning, middle and end of titration. At the very beginning of titration, when the solution contains only a weak acid, the quantity $b$ is equal to zero and the solution is sufficiently acid to allow us to neglect $c_{OH^-}$. Hence Eq. (18.88) becomes

$$c_{H_3O^+}=K_d\frac{a-c_{H_3O^+}}{c_{H_3O^+}}$$

Solution of this equation with respect to $c_{H_3O^+}$ yields

$$c_{H_3O^+}=-\frac{1}{2}K_d+\sqrt{\frac{1}{4}K_d^2+aK_d} \tag{18.89}$$

For a very weak acid the values of $c_{H_3O^+}$ and $K_d$ are low, and the equation can be written as

$$c_{H_3O^+}=\sqrt{aK_d}$$

In the middle of titration of a weak acid with a strong base, i.e. at pH $\geqslant 4$, we may neglect the difference $c_{H_3O^+} - c_{OH^-}$ and Eq. (18.88) becomes

$$pH = pK_d + \log \frac{b}{a-b} \tag{18.90}$$

At the end of titration, i.e. at the equivalent point, we have $a = b$ and the quantity $c_{H_3O^+}$ may be neglected, since the solution has an alkaline reaction owing to the hydrolysis of the formed salt of the weak acid and strong base, and Eq. (18.88) becomes

$$c_{H_3O^+} = K_d \frac{c_{OH^-}}{a - c_{OH^-}}$$

Substituting the ratio $K_w/c_{H_3O^+}$ for $c_{OH^-}$ and solving the quadratic equation obtained, we get

$$c_{H_3O^+} = \frac{K_w}{2a} + \sqrt{\frac{K_w^2}{4a^2} + \frac{K_d K_w}{a}}$$

The fraction $K_w/2a$ is usually very small and it may be neglected. Hence

$$c_{H_3O^+} = \sqrt{\frac{K_d K_w}{a}} \quad \text{or} \quad pH = \frac{1}{2} pK_w + \frac{1}{2} pK_d + \frac{1}{2} \log a \tag{18.91}$$

The simplified equations given above allow us to calculate the entire titration curve from its beginning to the equivalent point. If neutralization is half through, i.e. if $b = 0.5a$, Eq. (18.90) becomes

$$pH = pK_d$$

Thus, by measuring the pH when neutralization is half through, we can find the approximate value of the dissociation function for a weak acid.

3. If an acid is very weak, for example if phenol is being titrated, the pH of a 0.1 $N$ solution of this acid is still higher, and in the course of the addition of a base the pH becomes greater than seven long before the equivalent point is reached. But in this case also, as shown in Fig. 18.4, a buffer solution is formed. When from two to eight cubic centimetres of the alkali are added, the pH of the solution grows at a much slower rate than at the beginning and end of titration, when the equivalent point is near. The titration curve for such acids has no vertical portion like the ones in the preceding examples, and titration is conducted with a standard solution.

4. In the titration of weak bases with strong acids the same laws are observed as in Examples 2 and 3. The only difference is that the pH does not grow, but decreases as shown in Fig. 18.5. The pH is calculated in the same way as in the titration of a weak acid with a strong base, except that in the equation corresponding to Eq. (18.88) the quantities $c_{H_3O^+}$ and $c_{OH^-}$ exchange places.

5. If a mixture of two acids considerably differing in strength is titrated, for example a solution containing hydrochloric and acetic

acids, two sharply rising portions are observed on the titration curve (Fig. 18.6). The first one, beginning at a small value of pH, corresponds to the neutralization of the strong acid; the further change in the pH depends entirely on the neutralization of the weak acid. In such titration two indicators must be used, one of which, for example when titrating the acids $HCl + CH_3COOH$, changes its colour in the range of pH values from 3 to 4, and the second from 8 to 10.

A glance at Table 18.6 shows that methyl orange and phenolphthalein will be a good combination here. The latter is colourless in an acid medium and does not hamper observation of the change in the colour of the methyl orange from red to yellow. At the end of titration of the weak acid, the red colour of the phenolphthalein is clearly seen on the yellow background. A different combination of indicators may also be used, of course.

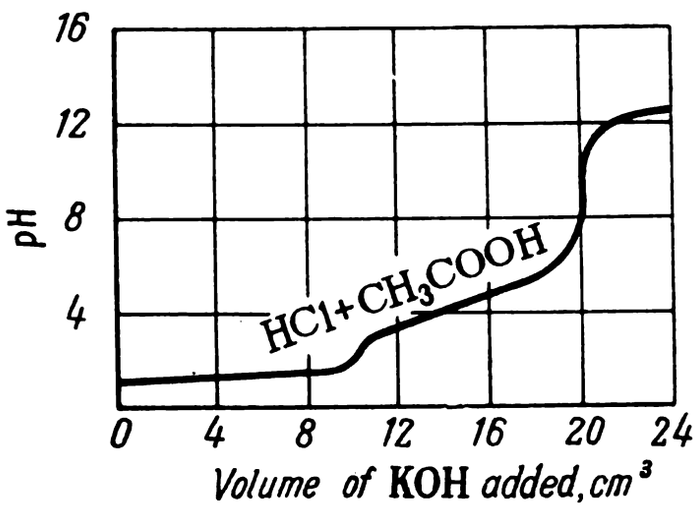



Fig. 18.6. Titration curve for mixture of strong and weak acids

The possibility of the separate titration of a mixture of two acids is calculated according to Eq. (18.81) given above:

$$\frac{k_{II}}{k_I} = \frac{[A_{II}^-][HA_I]}{[A_I^-][HA_{II}]}$$

but in the given case the quantities $k_I$, $[HA_I]$, $[A_I^-]$ and $k_{II}$, $[HA_{II}]$, $[A_{II}^-]$ relate to two coexisting acids. The influence of water, in view of the fact that its dissociation function is much smaller than $k_I$ and $k_{II}$, may be neglected.

Assume that $k_I = 10^{-10}$ and $k_{II} = 10^{-5}$ and that at the beginning of titration the concentrations of both acids are 1 $N$. Let us see whether it is possible to determine by titration the content of each of the acids with an accuracy up to 0.1%. For this purpose it is necessary that when a residual concentration of the stronger acid equal to 0.001 $N$ is reached, the concentration of the combined weaker acid should be considerably lower than 0.001 $N$. The concentration $[A_I^-]$ at the moment of completion of titration of the acid $[HA_{II}]$ is calculated by Eq. (18.81):

$$\frac{10^{-5}}{10^{-10}} = \frac{1 \times 1}{0.001[A_I^-]} \quad \text{and} \quad [A_I^-] = 10^{-2}$$

The calculation shows that the desired accuracy is unattainable, since by the moment when $[A_{II}^-]$ reaches 0.001 $N$ the consumption of the base for the other acid is 0.01 g-eq/dm$^3$. The required accuracy of separation of acids of the given

concentration is possible only with a greater difference between the values of the dissociation function. For example, when $k_{II} = 10^{-5}$ the value of $k_I$ should be $10^{-12}$ or less.

6. In the titration of a weak acid with a weak base in an aqueous medium, the titration curve has no vertical section and passes the equivalent point at a pH depending on the ratio of the acid and base strengths, but in general not far from pH = 7. Such titration, as that of a very weak acid described above, requires a specially prepared standard for each separate case.

Owing to hydrolysis of the weak acid and weak base, the complete equation relating the composition of a solution and its pH is a quartic one relative to $c_{H_3O^+}$. For this reason it is very difficult to plot an exact titration curve. Approximate equations, however, make it possible to plot a titration curve with a satisfactory accuracy.

The pH at the initial moment is determined by Eq. (18.89). The pH from the beginning of titration to neutralization of the acid by 90% is calculated according to the same equations used for the titration of a weak acid with a strong base. As long as the amount of free acid is not less than 10%, the influence of hydrolysis may be neglected.

The pH at the equivalent point, i.e. in the solution of hydrolyzed salt, can be found by Eq. (18.75):

$$k_{HA} = \frac{c_{H_3O^+} c_{A^-}}{c_{HA}}$$

whose transformation gives Eq. (18.76) which also holds after hydrolysis of the acid

$$c_{H_3O^+} = k_{HA} \frac{c_{HA}}{c_{A^-}} = k_{HA} \frac{c\beta}{c(1-\beta)} = k_{HA} \frac{\beta}{1-\beta}$$

According to Eq. (18.61), the fraction $\beta/(1-\beta)$ is equal to $\sqrt{K_{hydr}}$, so that by using Eq. (18.62) we get

$$c_{H_3O^+} = k_{HA} \sqrt{K_{hydr}} = k_{HA} \sqrt{\frac{k_w}{k_{HA} k_B}} = \sqrt{k_w \frac{k_{HA}}{k_B}}$$

or after taking logarithms

$$pH = \frac{1}{2} pk_w + \frac{1}{2} pk_{HA} - \frac{1}{2} pk_B \qquad (18.92)$$

If the dissociation functions of a weak acid and a weak base are approximately equal, i.e. $pk_{HA} \approx pk_B$, then $pH = \frac{1}{2} pk_w$. In this case, notwithstanding hydrolysis, the reaction of the solution is neutral. If $k_{HA} > k_B$, the solution has an acid reaction. If $k_{HA} < k_B$, the solution has an alkaline reaction.

Since Eq. (18.92) for the pH of a solution at the equivalent point contains only constants, it may be assumed that in the first approximation the pH of a solution of a salt of a weak acid and weak base does not depend on the concentration.

7. In the neutralization of a dibasic acid with a strong base two alternatives are possible. If the first stage of dissociation of such an acid corresponds to the dissociation of a strong acid, and the second one to that of a weak acid, titration of such an acid, for example chromic acid, proceeds in the same way as titration of a mixture of a weak and a strong acids. If both stages of dissociation correspond to acids almost identical in strength, the titration curves will be superposed, since the base is simultaneously distributed between both acids. In this case it is impossible to determine quantitatively the content of the acid in the solution by the method of titration. There nevertheless does exist a certain relation between the amount of base added and the pH of the solution, and this relation can be calculated.

8. When the inflections of titration curves for mixtures of acids and bases close in strength are not sharp enough, water may be replaced by a correspondingly selected protogenic solvent, for example acetic acid. The strength of the acids decreases, but not identically, so that the difference between the strengths grows, and when they are titrated together sharper inflections are observed on the pH curve. For this reason the colour of the indicator changes within the limits of a smaller amount of base added. This makes it possible to find more accurately the equivalent points corresponding to the completion of titration of each of the acids of the mixture.

The difference between the strengths of bases can be increased in the same way by correspondingly selecting the solvent, so as to determine their concentration by titration.

**18.16. Amphoteric Electrolytes.** Electrolytes that can simultaneously display the properties of an acid and a base are called *amphoteric electrolytes* or *ampholytes*. The hydroxides of such metals as zinc and aluminium may be included among them. Such hydroxides can dissociate according to the equations

$$Zn(OH)_2 + 2H_2O = ZnO_2^{2-} + 2H_3O^+$$

and

$$Zn(OH)_2 = Zn^{2+} + 2(OH)^-$$

In this case both the acid and basic functions are determined by the properties of the same group $OH^-$. But there are also ampholytes of another kind. Their acid and basic properties are determined by the presence of two different functional groups. Amino acids $NH_2RCOOH$ are the most characteristic example of this kind of compounds. Amino acids enter into the composition of proteins.

For this reason investigation of the latter is impossible without taking account of the phenomena due to the amphoteric properties of amino acids.

It would seem that the carboxyl group of an amino acid should have protogenic properties, and the amino group protophilic ones. In investigating aqueous solutions of amino acids of the fatty series, however, it was found that their Raman spectrum does not give lines corresponding to the carboxyl group COOH. This line appears only after the addition of a strong acid, which, having high protogenic properties, gives up a proton to the amino acid. These experimental data indicate that in an aqueous solution the molecules of fatty amino acids completely or almost completely change to the form $NH_3^+RCOO^-$, i.e. are ions simultaneously carrying both a positive and a negative charges. This is also confirmed by the fact that the relative permittivity of aqueous solutions of these amino acids is very high, and this means that the solution contains particles with great dipole moments. The ions $NH_3^+RCOO^-$, called *amphoteric ions* or *amphions*, belong to such particles. They are also called *dual ions* or *zwitter-ions*.

Bounding a proton in reaction with a protogenic substance, the group $COO^-$ of an amphion displays basic properties, while the group $NH_3^+$, giving up a proton to a protophilic base, displays acid properties:

$$NH_3^+RCOO^- + H_3O^+ = NH_3^+RCOOH + H_2O$$

$$NH_3^+RCOO^- + OH^- = NH_2RCOO^- + H_2O$$

The investigation of amino acids is appreciably simplified if we consider ions of the type $NH_3^+RCOOH$ as dibasic acids, for which the first stage of dissociation is that of the carboxyl group:

$$NH_3^+RCOOH + H_2O = NH_3^+RCOO^- + H_3O^+$$

and the second stage is dissociation of the amino group:

$$NH_3^+RCOO^- + H_2O = NH_2RCOO^- + H_3O^+$$

A different dissociation constant corresponds to each stage:

$$K_{d_I} = \frac{a_{NH_3^+RCOO^-} a_{H_3O^+}}{a_{NH_3^+RCOOH}} \quad \text{and} \quad K_{d_{II}} = \frac{a_{NH_2RCOO^-} a_{H_3O^+}}{a_{NH_3^+RCOO^-}} \tag{18.93}$$

For approximate calculation of the dissociation constants of amino acids, Eqs. (18.93) are used after substituting the concentrations for the activities in them. Taking logarithms of these equations, we get

$$\log K_{d_I} \approx \log k_{NH_3^+RCOOH} = -pH + \log \frac{[NH_3^+RCOO^-]}{[NH_3^+RCOOH]} \tag{18.94}$$

$$\log K_{d_{II}} \approx \log k_{NH_3^+RCOO^-} = -pH + \log \frac{[NH_2RCOO^-]}{[NH_3^+RCOO^-]} \tag{18.95}$$

The ionic strength of the solutions is not great as a rule, and all the activity coefficients are close to unity. For this reason such a simplification does not lead to a big error. The pH in Eqs. (18.94) and (18.95) is measured by the e.m.f. method. To determine the concentrations in Eq. (18.94), it is necessary to know the total concentration $a$ of the amino acid and the concentration $c$ of the strong acid added. Hence

$$[NH_3^+RCOO^-]=a-c \quad \text{and} \quad [NH_3^+RCOOH]=c$$

In Eq. (18.95) the quantities $[NH_3^+RCOO^-] = a - b$ and $[NH_2RCOO^-] = b$, where $b$ is the concentration of the strong base added.

The quantities $K_{d_I}$ and $K_{d_{II}}$, which are the dissociation constants of two consecutive stages, differ by several orders (see Tables 18.12 and 18.13).

TABLE 18.12

**Dissociation Constants for Dibasic Organic Acids at 25 °C**

| Acid | $pK_{dI}$ | $pK_{dII}$ | Acid | $pK_{dI}$ | $pK_{dII}$ |
|---|---|---|---|---|---|
| Oxalic | 1.30 | 4.286 | Pimelic | 4.51 | 5.42 |
| Malonic | 2.84 | 5.696 | Suberic | 4.53 | 5.40 |
| Succinic (amber) | 4.20 | 5.60 | Maleic | 2.00 | 6.27 |
| Glutaric | 4.35 | 5.42 | Fumaric | 3.03 | 4.48 |
| Adipinic | 4.42 | 5.41 | Phthalic | 2.89 | 5.42 |

TABLE 18.13

**Dissociation Constants for Amino Acids at 25 °C**

| Acid | $pK_{dI}$ | $pK_{dII}$ | Acid | $pK_{dI}$ | $pK_{dII}$ |
|---|---|---|---|---|---|
| Alanine | 2.340 | 9.870 | Histidine | 1.77 | 9.18 |
| | | 9.04 | Diglycine | 3.15 | 8.10 |
| Arginine | 2.02 | 12.48 | Isoleucine | 2.318 | 9.758 |
| Asparaginic | 2.09 | 9.82 | Leucine | 2.328 | 9.744 |
| | 3.87 | | Norleucine | 2.335 | 9.833 |
| Valine | 2.287 | 9.719 | Oxyproline | 1.92 | 9.73 |
| Glutaminic | 2.19 | 9.66 | Tryptophan | 2.38 | 9.39 |
| | 4.28 | | | | |

Sometimes, for example in the investigation of proteins, it is necessary to create conditions in which an amino acid dissociates

producing the same concentration of the positive ($NH_3^+RCOOH$) and the negative ($NH_2RCOO^-$) ions. In pure water such a condition cannot be complied with, since the dissociation constants for the two stages are not the same. To intensify one stage of dissociation and suppress the other, the corresponding hydrogen ion concentration must be created in the solution. This is done by adding either an acid or a base. The pH at which an ampholyte produces the same concentrations of positive and negative ions is called the *isoelectric point*. At this point the following condition is obviously observed:

$$[NH_3^+RCOOH] = [NH_2RCOO^-] \tag{18.96}$$

Summation of Eqs. (18.94) and (18.95) gives

$$\log K_{d_I} K_{d_{II}} = -2pH + \log \frac{[NH_3^+RCOO^-]}{[NH_3^+RCOOH]} \frac{[NH_2RCOO^-]}{[NH_3^+RCOO^-]} \tag{18.97}$$

With account to Eq. (18.96), we get

$$\log K_{d_I} K_{d_{II}} = -2pH \quad \text{or} \quad a_{H^+} = \sqrt{K_{d_I} K_{d_{II}}}$$

In Eq. (18.97) the concentrations have been substituted for the activities. The error is quite small, since $f_{NH_3^+RCOO^-}$ cancel out, while although $f_{NH_3^+RCOOH}$ and $f_{NH_2RCOO^-}$ are not equal to unity, they are very close in value.

**18.17. Solubility Product.** Let us consider the relation between the activities of the ions of a binary strong poorly soluble electrolyte, for example AgCl, in its saturated solution. At equilibrium the following equation is observed:

$$\mu_{AgCl(s)} = \mu_{Ag^+} + \mu_{Cl^-}$$

The left-hand part of the equation is constant for a given temperature, and therefore in a saturated solution

$$\mu_{Ag^+} + \mu_{Cl^-} = \text{const}$$

Expressing the quantities $\mu$ through the activities, we get

$$\mu^\circ_{Ag^+} + RT \ln a_{Ag^+} + \mu^\circ_{Cl^-} + RT \ln a_{Cl^-} = \text{const} \tag{18.98}$$

or

$$a_{Ag^+} a_{Cl^-} = \exp\left(\frac{\text{const} - \mu^\circ_{Ag^+} - \mu^\circ_{Cl^-}}{RT}\right) = K_{ap}$$

The quantity $K_{ap}$, which is constant at a given temperature, is called the *activity product*.

For a saturated solution of a salt, $K_{ap}$ should always be constant at a given temperature:

$$K_{ap} = a_{Ag^+} a_{Cl^-} = [Ag^+][Cl^-] f_{Ag^+} f_{Cl^-} = [Ag^+][Cl^-] f_\pm^2 \tag{18.99}$$

A solution of a poorly soluble salt is a dilute solution. If such solutions contain no other substances increasing their ionic strength, the activities may be replaced by the concentrations:

$$[Ag^+][Cl^-] = K_{sp} \tag{18.100}$$

The quantity $K_{sp}$ is called the *solubility product.*

Table 18.14 gives the solubility products for selected salts that are poorly soluble in water at 25 °C.

TABLE 18.14

**Solubility Products for Selected Salts Dissolved in Water at 25 °C**

| Salt | $K_{sp}$ | Salt | $K_{sp}$ |
|---|---|---|---|
| AgCl | $1.56 \times 10^{-10}$ | $Ag_2CO_3$ | $6.2 \times 10^{-12}$ |
| AgBr | $7.7 \times 10^{-13}$ | $PbSO_4$ | $1.6 \times 10^{-8}$ |
| AgI | $1.5 \times 10^{-16}$ | $CaSO_4$ | $6.26 \times 10^{-5}$ |
| $Ag_2S$ | $5.9 \times 10^{-52}$ | $BaSO_4$ | $9.9 \times 10^{-11}$ |
| $Hg_2Cl_2$ | $1.15 \times 10^{-18}$ | $Hg_2SO_4$ | $4.7 \times 10^{-7}$ |
| $Hg_2Br_2$ | $5.50 \times 10^{-23}$ | MnS | $1.1 \times 10^{-15}$ |
| $Hg_2I_2$ | $4.95 \times 10^{-29}$ | FeS | $3.8 \times 10^{-20}$ |
| $Hg_2(CN)_2$ | $5.0 \times 10^{-40}$ | ZnS | $7.4 \times 10^{-27}$ |
| $Hg_2CO_3$ | $9.0 \times 10^{-17}$ | CdS | $1.2 \times 10^{-28}$ |
| $CaCO_3$ | $4.82 \times 10^{-9}$ | PbS | $6.7 \times 10^{-29}$ |
| $BaCO_3$ | $4.93 \times 10^{-9}$ | CuS | $3.2 \times 10^{-38}$ |
| $PbCO_3$ | $7.24 \times 10^{-14}$ | $Hg_2S_2$ | $1 \times 10^{-45}$ |

In aqueous solutions of AgCl the concentrations of the ions are the same:

$$[Ag^+] = [Cl^-] \tag{18.101}$$

Denoting $[Ag^+]$ and $[Cl^-]$ by $c$, we find that $K_{sp} = c^2$ or $c = \sqrt{K_{sp}}$. If a salt is added to the solution which when dissolved produces the ions $Ag^+$ or $Cl^-$, for example $AgNO_3$ or KCl, Eq. (18.101) does not hold. Let us consider this case without taking $f_\pm$ into account. Thus, if there is an excess of the ions $Cl^-$ and their concentration has grown from $c$ to $c + x$, the equation $K_{sp} = c(c + x)$ should be observed, which at $x \gg c$ becomes $K_{sp} = cx$. The greater the value of $x$, the smaller is that of $c$. Thus, as the ion $Cl^-$ is added, saturation of the solution by the salt AgCl sets in at lower and lower values of the concentration $c$. If the ion $Cl^-$ is introduced into an already saturated solution of the salt AgCl, the salt freezes out in the form of the crystalline phase. The same result is obtained upon the addition of $AgNO_3$. Below is given an approximate calculation showing

how the solubility $c$ of the salt AgCl depends on the concentration $x$ of the added salt (KCl or $AgNO_3$). At 25 °C for AgCl we have $K_{sp} = 1.56 \times 10^{-10}$, but for purposes of illustration we shall assume that $K_{sp} = 1 \times 10^{-10}$. In pure water $c = [Ag^+] = [Cl^-]$, whence $c = \sqrt{10^{-10}} = 10^{-5}$. The equality $K_{sp} = 1 \times 10^{-10}$ should also be observed after a salt with the same ion is added. The values of $c$ for various values of $x$ are given below:

| | | | | | | |
|---|---|---|---|---|---|---|
| $x$ . . . . . | 0 | 0.00001 | 0.0001 | 0.001 | 0.01 | 0.1 |
| $c$ . . . . . | $1 \times 10^{-5}$ | $6.2 \times 10^{-6}$ | $1 \times 10^{-6}$ | $1 \times 10^{-7}$ | $1 \times 10^{-8}$ | $1 \times 10^{-9}$ |

Even if only 0.001 mol/dm³ of KCl or $AgNO_3$ is added, the solubility of AgCl decreases to one-hundredth of the original value. For this reason it is accepted practice in quantitative analysis to wash precipitates not with pure water, but with water containing a certain amount of a precipitating reagent. For example, a precipitate of AgCl is washed with a solution of HCl.

The ratio of the solubility products determines equilibrium between two poorly soluble salts. Let us consider the reaction

$$AgCl(s) + I^- = AgI(s) + Cl^- \qquad (18.102)$$

The equilibrium constant of this reaction

$$K_c = \frac{[Cl^-]}{[I^-]} = \frac{[Cl^-][Ag^+]}{[I^-][Ag^+]} = \frac{K_{sp,\,AgCl}}{K_{sp,\,AgI}}$$

The quantities $K_{sp,\,AgCl} = 1.56 \times 10^{-10}$ and $K_{sp,\,AgI} = 1.5 \times 10^{-16}$. Hence $K_c = 1.04 \times 10^6$. Therefore according to Eq. (18.102) the reaction will proceed from the left to the right even at a concentration $[I^-]$ that is one-millionth of $[Cl^-]$. Thus a poorly soluble salt displaces a more soluble one from a precipitate.

The solubility product for more complex electrolytes is found in the same way. For example, for $Ag_2S$ we have $K_{sp} = [Ag^+]^2[S^{2-}]$ or $K_{sp} = (2c)^2c = 4c^3$. If $H_2S$ has been added to the solution and the concentration of its dissociated part is $x$ mol/dm³, then $K_{sp} = (2c)^2(c + x)$. When $x \gg c$, then $K_{sp} = 4c^2x$. When $x$ mol/dm³ of ionized $AgNO_3$ are added to a solution of $Ag_2S$, the quantity $[Ag^+] = 2c + x$ and $[S^{2-}] = c$, whence $K_{sp} = (2c + x)^2 c$. When $x \gg c$ we have $K_{sp} = x^2c$.

When like ions are added, soluble complexes are sometimes formed whose composition includes a poorly soluble salt. Such "solubility" has nothing in common with the solubility being considered in this section, which depends on the concentration of each of the ions of the poorly soluble salt.

Complexes are formed, for example, upon the addition of ions $CN^-$ to AgCN or ions $I^-$ to $HgI_2$. The complex ions $Ag(CN)_2^-$ and $HgI_3^-$ are formed, as a result of which the concentration of the ions

$Ag^+$ or $Hg^{2+}$ in the solution decreases, and the product $[Ag^+][CN^-]$ or respectively $[Hg^{2+}][I^-]^2$ will be smaller than the solubility product. The violated equilibrium is restored as a result of the dissolving of the poorly soluble salt in the precipitate.

Soluble complex compounds are also formed when unlike ions are introduced into a solution. For example, the solubility of AgI grows when $Na_2S_2O_3$ is added, since a complex ion is formed:

$$Ag^+ + 2S_2O_3^{2-} = [Ag(S_2O_3)_2]^{3-}$$

Measuring the dissociation constant of this complex ion by the e.m.f. method and knowing the solubility product of AgI, we can compute the solubility of AgI in the presence of $Na_2S_2O_3$:

$$k_c = \frac{[Ag^+][S_2O_3^{2-}]^2}{[Ag(S_2O_3)_2]^{3-}} = 1.02 \times 10^{-13}$$

$$K_{sp,\,AgI} = [Ag^+][I^-] = 1.5 \times 10^{-16}$$

whence

$$[Ag(S_2O_3)_2]^{3-}[I^-] = [S_2O_3^{2-}]^2 \times 1.47 \times 10^{-3}$$

But $[Ag(S_2O_3)_2]^{3-} = [I^-]$, since the concentration of the free ions of silver is very low, and the concentration of the free iodide ions is equal to that of the silver ions practically completely combined in a soluble complex. Therefore each of the concentrations $[I^-]$ and $[Ag(S_2O_3)_2]^{3-}$ is equal to the number of gramme-equivalents of the salt AgI that has passed into the solution. This concentration is denoted, as previously, by the letter $c$. From Eq. (18.103) we have

$$c^2 = [S_2O_3^{2-}]^2 \times 1.47 \times 10^{-3} \quad \text{or} \quad c = 3.8 \times 10^{-2}[S_2O_3^{2-}]$$

which corresponds to experimental data. This reaction of transferring the salt AgCl (or AgBr) into solution is used in photography for fixing negatives and prints.

It was assumed in all the previous examples that the activity coefficient of the dissolved ions is equal to unity, and instead of the activity product [Eq. (18.99)] we used the solubility product [Eq. (18.100)]. For more concentrated solutions the activity coefficient can no longer be taken equal to unity, and the activity product should be used.

The addition of a foreign salt to a solution increases its ionic strength and reduces the activity coefficient of the salt that was in solution before the foreign salt was added. The decrease of the activity coefficient leads to a growth of the solubility of the salt present in the original solution, since the activity of crystals is constant.

The values of the activity products are of great practical importance, in particular in chemical technology and in analytical chemistry, since they determine the conditions in which the dissolving of salts or their falling out from solutions should occur. The forma-

tion of precipitates is possible only when the product of the activities of the ions present exceeds the value of $K_{ap}$.

The activity (or solubility) product can be measured the most accurately by the e.m.f. method. The solubility is also frequently determined by measuring the electrical conductivity of saturated solutions. This method, however, can be used only for solutions of a pure salt.

If the measured activity products are very low, they cannot be considered as ordinary thermodynamic properties of the system. For CuS, for instance, $K_{ap} = 10^{-38}$, which approximately corresponds to 120 ions per cubic decimetre of solution. Thermodynamic laws cannot be applied to such small numbers of particles. The small number of particles is only of a statistical importance, as the mean value during a certain time interval.

# ELECTROMOTIVE FORCES. CHEMICAL SOURCES OF CURRENT

## CHAPTER 19

## ELECTROCHEMICAL CELLS. ELECTROMOTIVE FORCE

**19.1. General.** It is general knowledge that when an electric current flows through an electrolyte, electrochemical reactions proceed on the surface of the electrodes. They are accompanied by the migration of electrons to or from an electrode. In the previously considered examples, the electrochemical reactions were induced by an external source of current. The reverse phenomenon is also possible, however, namely, electrochemical reactions proceeding on two different surfaces of contact of electronic and electrolytic conductors give birth to an electric current (the immersion of two electrodes into an electrolyte is the reason why a current flows along the metal conductor connecting the electrodes). Electrochemical reactions on electrodes causing a current to flow in a conductor proceed only when the electrodes are connected (when the current flows) and stop when they are disconnected.

It should be remembered that there is frequently dynamic equilibrium between an electrode and a solution. Here the electrochemical reaction at the electrodes proceeds in both directions at the same rate even without closing of the circuit, without producing a macroscopic effect. These exchange currents can be detected with the aid of isotope indicators (see Sec. 24.2).

An *electrochemical* (or *galvanic*) cell is a device (set-up) for producing an electric current as a result of electrochemical reactions. The historical term *galvanic cell* is equivalent to the term *electrochemical cell* used more generally at present. The simplest electrochemical cell consists of two metal electrodes (electronic conductors) immersed

in an electrolyte (electrolytic conductor) and connected to each other by means of a metal conductor. Several identical cells connected in series form a battery.

Systems are possible that cannot be used as chemical sources of current, but in which a current is produced as a result of electrochemical reactions having the same mechanism as in ordinary cells. These include the microcells forming on the surface of metals and alloys upon their corrosion in electrolytes.

A most important quantitative characteristic of a cell is the *electromotive force* (e.m.f.) $E$, equal to the difference of potentials of a properly disconnected cell, i.e. to the difference of potentials across the ends of electronic conductors made of the same material and connected to the extreme electrodes of the cell. The sign of the e.m.f. coincides with that of the total potential difference of the cell or is opposite to it depending on the sign convention used.

If the same reaction proceeds on the surface of an electrode, but in opposite directions when the direction of the current is reversed, such electrodes, and also a cell containing them, are called *reversible*. The e.m.f. of a reversible cell is a thermodynamic property of it, i.e. it depends only on the temperature, pressure, nature of the electrodes and of the electrolyte of the cell, and the concentration of the electrolyte. An example of a reversible cell is the Daniell-Jacobi one

$$(-)Cu \mid Zn \mid ZnSO_4, aq \parallel CuSO_4, aq \mid Cu(+)$$ [1]

in which each electrode is reversible, since when the current is reversed, the reverse reactions proceed on the electrodes.

When the cell is functioning, the following reactions proceed on the electrodes: $Zn \rightarrow Zn^{2+} + 2e$ and $2e + Cu^{2+} \rightarrow Cu$.

When an infinitely small current from an external source is passed through the cell, the following reactions proceed on the electrodes: $Zn^{2+} + 2e \rightarrow Zn$ and $Cu \rightarrow Cu^{2+} + 2e$.

The Volta cell

$$(-)Zn \mid H_2SO_4 \mid Cu(+)$$

is irreversible.

When the cell is functioning, the following electrode reactions proceed: $Zn \rightarrow Zn^{2+} + 2e$ and $2H^+ + 2e \rightarrow H_2$.

When an infinitely small current from an external source is passed through the cell, the electrode reactions will be $2H^+ + 2e \rightarrow H_2$ and $Cu \rightarrow Cu^{2+} + 2e$.

Any electrochemical cell as a whole is never in equilibrium. In an irreversible cell a chemical reaction may proceed even if the elec-

[1] Here the single vertical bar signifies a phase boundary, and the double vertical bar the junction between two solutions belonging to two electrode systems (half-cells).

trodes are not connected externally (the reaction $Zn + H_2SO_4$ in the Volta cell). But a reversible cell (in the above meaning) as a whole is also far from thermodynamic equilibrium. If such a cell is closed through an external finite resistor and not interfered with, a measurable current will appear in the external circuit, i.e. the cell performs work and irreversibly approaches equilibrium. A disconnected cell remains unchanged only temporarily. For example, in the disconnected Daniell-Jacobi cell the ions $Cu^{2+}$ diffuse through the solution to the zinc electrode. When the latter comes into contact with the copper ions, an irreversible (without the performance of work) reaction of displacement of the $Cu^{2+}$ ions from the solution by the metal zinc occurs, i.e. the same reaction that serves as a source of current when the cell functions.

The e.m.f. of an electrochemical cell consists of the potential differences between the different conductors of the open cell at the places of their contact (these potential differences are also called *potential jumps*). The contact of electronic conductors leads to the origination of a potential difference called the *metal-metal contact* or *Galvani potential* (see Sec. 20.1).

The basic electrochemical phenomena are processes proceeding at the interfaces between different phases. The work of a cell and its e.m.f. are only the summary manifestation of a complex of processes proceeding on phase interfaces. This is why theoretical electrochemistry devotes its main attention to investigating the molecular processes on phase interfaces that cause the appearance of potential jumps and, therefore, e.m.f.s at these interfaces. It is usually impossible to measure separate potential jumps, however, and only the e.m.f.s are measured.

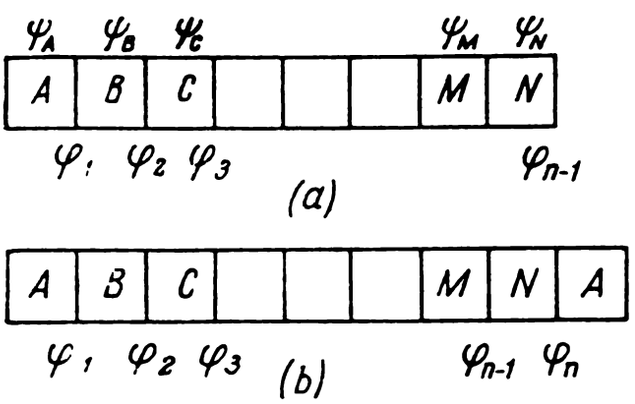



Fig. 19.1. Circuits of conductors: *a*—improperly disconnected; *b*—properly disconnected

**19.2. Potential Jumps and E.M.F.** It is known from experience that when two chemically or physically different conductors come into contact, they are electrified differently. A potential jump occurs on the surface of contact of the conductors whose value depends neither on the shape nor on the dimensions of the conductors and the area of their contact, but does depend on the chemical nature and physical state of the conductors.

Suppose we have a circuit formed of conductors A, B, C, . . ., M and N (Fig. 19.1*a*):

$$\underset{\varphi_1}{A \mid B} + \underset{\varphi_2}{B \mid C} + \ldots + \underset{\varphi_{n-1}}{M \mid N} \qquad \text{(a)}$$

Here A | B, B | C are the potential differences (jumps) at the interfaces of the contacting conductors, and the symbol A | B shows the potential difference (jump) between conductors A and B, i.e. $A \mid B = \varphi_1$. If the potentials of A, B, . . ., N are respectively denoted by $\psi_A, \psi_B, \ldots, \psi_N$, then $A \mid B = \varphi_1 = \psi_B - \psi_A$, $B \mid C = \varphi_2 = \psi_C - \psi_B$, and so on. It is quite obvious that the sum of all the potential jumps at all the interfaces of circuit (a) is equal to the difference of potentials between conductors A and N at the two ends of the circuit, namely

$$E = \sum^{n} \varphi_{n-1} = \psi_N - \psi_A$$

The quantity $E$ is called the *e.m.f.* of a circuit of conductors.

Let us consider a circuit having the same conductor at its beginning and end (Fig. 19.1*b*). Such a circuit is called a *properly disconnected one*. There is no sense of speaking of a properly disconnected circuit consisting of two conductors, since its e.m.f. ($E = A \mid B - B \mid A$) is always equal to zero[1]. If a properly disconnected circuit consists of three or more conductors, then with respect to the e.m.f. it is necessary to distinguish between circuits consisting only of electronic conductors and ones that also include electrolytic conductors.

For electronic conductors we have

$$E = A \mid B + B \mid C + \ldots + M \mid N + N \mid A = 0 \qquad \text{(b)}$$

consequently

$$A \mid B + B \mid C + \ldots + M \mid N = A \mid N \qquad \text{(c)}$$

i.e. *the e.m.f. of a circuit consisting of only electronic conductors is equal to the jump of potentials between the first and the last conductors when they are directly connected* (Volta's law). If the circuit is properly disconnected, then, as indicated above, its e.m.f. is equal to zero.

An essential condition for the e.m.f. of a circuit of electronic conductors to equal zero is the equality of the temperatures of all the contacts between the different conductors. If this condition is not observed, thermoelectromotive forces appear that are not dealt with in this course.

Volta's law cannot be applied to a properly connected circuit of conductors containing at least one electrolyte (S), i.e.

$$E = A \mid S + S \mid B + B \mid A \neq 0 \qquad \text{(d)}$$

$$E = A \mid S_1 + S_1 \mid S_2 + S_2 \mid B + B \mid A \neq 0 \qquad \text{(e)}$$

Obviously, only circuits of conductors including at least one electrolytic conductor are electrochemical cells. The Daniell-Jacobi

[1] It is clear that $A \mid B = -B \mid A$, since $\mid B \mid A \mid = \psi_A - \psi_B = -(\psi_B - \psi_A)$.

cell mentioned above can serve as an example of an electrochemical cell:

$$(-)Cu \mid Zn+Zn \mid ZnSO_4, aq+ZnSO_4, aq \parallel CuSO_4, aq+CuSO_4, aq \mid Cu(+)$$

or more briefly

$$(-)Cu \mid Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu(+)$$

(the terminals of the cell serve as the identical ends of the circuit)[1].

Let us note another important circumstance. When an electrochemical cell is connected to instruments or appliances and is thus closed with wires of copper or another metal M, it can be written as

$$E = M \mid A+A \mid K+\ldots+L \mid B+B \mid M \qquad (f)$$

but

$$M \mid A+B \mid M = -(A \mid M+M, \ B) = -A \mid B = B \mid A \qquad (g)$$

whence it can be seen that the material of the connecting wires does not affect the value of the e.m.f.

**19.3. Signs of Cell E.M.F.s. Summation of E.M.F.s of Complex Cells.** The e.m.f. of a single electrochemical cell is a positive quantity, since it always corresponds to a definite spontaneously proceeding process producing positive work. A negative e.m.f. would correspond to the reverse process which cannot proceed independently. When forming a complex cell, the process in one of the elementary cells can be so directed that it will be accompanied by the expenditure of work from an external source (a non-spontaneous process). The work of another elementary cell in which a spontaneous process proceeds can be used for this purpose. The total e.m.f. of any complex cell is obviously equal to the difference between the e.m.f.s of the separate elementary cells, i.e. to the algebraic sum of positive and negative quantities. For this reason it is very important to take account of the signs of the e.m.f.s in accordance with the conventional rules when writing the set-up of a cell and calculating the magnitude of the e.m.f. corresponding to it.

The e.m.f. of a cell is considered to be positive if the cations migrate in the solution from the left-hand electrode to the right-hand one during functioning of the cell, and the electrons in the external circuit travel in the same direction. The right-hand electrode is charged positively relative to the left-hand one. If the set-up is so written that the cations in the electrolyte and the electrons in the

[1] In notation of this type the formula of the salt relates to its solution or melt. The frequently used symbol "aq" indicates an aqueous solution, for example $CuSO_4$, aq denotes an aqueous solution of copper sulphate.

external circuit travel from the right to the left, the e.m.f. of such a cell is negative. Complying with this condition, we can easily find the total e.m.f. of a complex cell formed of several constituents.

Let us write the Daniell-Jacobi cell as follows

$$(-)Cu \mid Zn \mid ZnSO_4, aq \parallel CuSO_4, aq \mid Cu(+) \qquad (I)$$

The e.m.f. in this case is obviously positive. It is equal to 1.087 V. If we write the set-up of this cell as follows:

$$(+)Cu \mid CuSO_4, aq \parallel ZnSO_4, aq \mid Zn \mid Cu(-)$$

then $E = -1.087$ V[1].

In the following we shall not include in the scheme of a cell, for purposes of simplicity, its metal contacts required for proper breaking of the circuit, although the e.m.f. of a cell always includes the Galvani potentials of these contacts (see Sec. 20.5, which gives the method of measuring electrode potentials).

The e.m.f. of the cell

$$(-)Zn \mid ZnSO_4, aq \parallel KCl, aq, AgCl(s) \mid Ag(+) \qquad (II)$$

in which the reaction $0.5Zn + AgCl(s) = 0.5Zn^{2+} + Ag(s) + Cl^-$ proceeds is equal to 0.985 V.

Connecting cells I and II in series without violating the sequence of writing them

$$(-)Zn \mid ZnSO_4, aq \parallel CuSO_4, aq \mid Cu(+)(-)Zn \mid$$
$$\mid ZnSO_4, aq \parallel KCl, aq, AgCl(s), \mid Ag(+) \qquad (I+II)$$

we get an e.m.f. equal to $E_{II} + E_I = 0.985 + 1.087 = 2.072$ V.

Let us connect cells I and II in series so that two zinc electrodes are in contact, i.e. write cell II in the reverse direction:

$$(-)[(+)Ag \mid AgCl(s), KCl, aq \parallel ZnSO_4, aq \mid$$
$$\mid Zn(-)(-)Zn \mid ZnSO_4, aq \parallel CuSO_4, aq \mid Cu(+)](+) .$$

For this combination $E = -E_{II} + E_I = -0.985 + 1.087 = 0.102$ V.

**19.4. Measurement of E.M.F.** To measure the equilibrium (reversible) value of the e.m.f. of an electrochemical cell, it is necessary that the process proceed infinitely slowly, i.e. that the cell function at an infinitely small current. This condition is complied with in the compensation method, in which the cell is connected in series against

[1] The minus sign before the quantity $E$ is a purely formal characteristic. A negative e.m.f. from a qualitative viewpoint does not differ in any respect from a positive one. The "plus" and "minus" signs only indicate the direction of the current.

Using the different signs of the e.m.f., we can easily calculate the e.m.f. of a complex cell as the algebraic sum of the constituent e.m.f.s.

an external potential difference, and the latter is so adjusted that there is no current in the circuit. Hence the external potential difference is equal to the e.m.f. of the cell.

Using the compensation method, we can directly measure the value of the e.m.f.

Figure 19.2 shows the arrangement of the instruments used in the absolute measurement of the e.m.f. according to J. Poggendorf's method (1841). Circuit $ABC$ includes source $A$ of direct current (for example, an accumulator), variable resistor $R_1$ and coulometer $V$.

Cell $E$ whose e.m.f. is to be measured is connected in parallel to points $c$ and $d$ of the circuit, and galvanometer $G$ is connected in series with this cell. A current flows through circuit $ABC$ whose intensity $I$ is controlled by varying the resistance of $R_1$ and is measured by means of coulometer $V$.

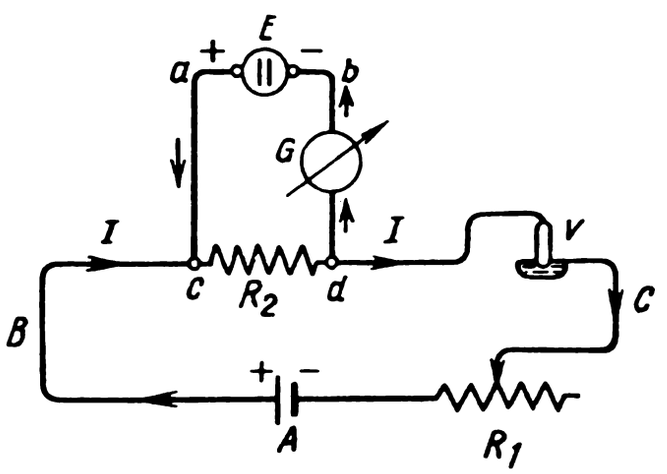



Fig. 19.2. Measurement of cell e.m.f. by Poggendorf's method

Along circuit $cEGd$ a current from cell $E$ flows in one direction, and a current from accumulator $A$ in the other. By changing the resistance of $R_1$, we can change the current intensity $I$ and the potential difference between points $c$ and $d$, which is determined according to Ohm's law, namely, $E = IR_2$. When this difference becomes equal to the e.m.f. of the cell, no current will flow along circuit $cEGd$ (on section $caEbGd$ the currents from $E$ and from $A$ flow in opposite directions, and the pointer of galvanometer $G$ does not deflect).

By measuring the current intensity $I_1$ in circuit $ABVC$ corresponding to the zero position of the pointer, we can find the potential difference $E_1 = I_1R_2$ between points $c$ and $d$ that is equal and opposite in sign to the e.m.f. of cell $E$, since the latter is disconnected when there is no current in the galvanometer.

The accurate determination of the e.m.f. of a cell according to Poggendorf's method is a quite complicated procedure. For this reason in laboratory practice it is preferred to compare the e.m.f. of a cell being studied with that of a so-called standard cell which is carefully measured at different temperatures. The comparison method is used for relative measurement of the e.m.f. of a cell. This method is also a compensation one. An arrangement for measuring the e.m.f. by the comparison method is shown in Fig. 19.3. Here $AB$ is a slide wire, i.e. a wire homogeneous in length having a considerable resistance. The wire can be stretched over a rule with a

scale or wound onto a drum whose number of revolutions is counted on a special scale. The ends of the slide wire are connected to a source of direct current (accumulator) $C$ whose e.m.f. is equal to $E_1$. The sliding contact on the wire is connected to its end $A$ through galvanometer $G$ and the cell $K$ being investigated whose e.m.f. $E$ is unknown. Both accumulator $C$ and cell $K$ are connected to the left end of the slide wire with their like poles. By moving the sliding contact (the position shown by point $D$ on slide wire $AB$) we seek such a position at which the pointer of the galvanometer will be at zero (i.e. there is no current in circuit $AKGD$). The potential differences between points $A$ and $D$ created by the two oppositely directed currents from sources $C$ and $K$ are therefore the same and equal to the e.m.f. of the cell $E$. This value is part of the accumulator e.m.f. $E_1$ proportional to the ratio $AD/AB$, and

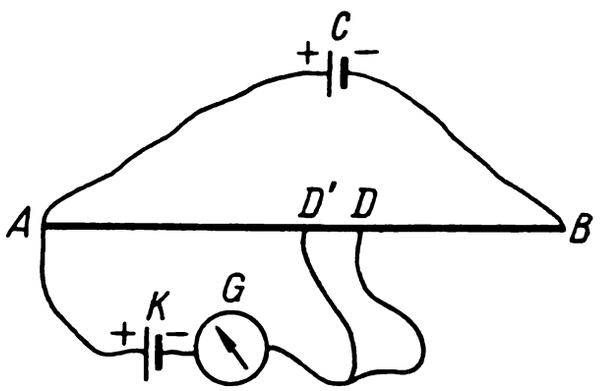



Fig. 19.3. Measurement of cell e.m.f. by method of Du Bois-Reymond and Clark

$$E = \frac{AD}{AB} E_1 \qquad \text{(a)}$$

If we now connect a standard cell with a known e.m.f. equal to $E_0$ instead of the cell $K$ being investigated, the position of the contact corresponding to the absence of current in the galvanometer will change, and will shift from point $D$ to point $D'$. Now

$$E_0 = \frac{AD'}{AB} E_1 \qquad \text{(b)}$$

From Eqs. (a) and (b) we have

$$E = E_0 \frac{AD}{AD'} \qquad \text{(c)}$$

Determination of the e.m.f. of a cell according to this method does not require measurement of the current and resistance or knowledge of the e.m.f. of the current source $C$. It is only necessary to have a standard cell and a slide wire $AB$, the resistance of any section of which would be strictly proportional to the length of this section.

Modern electrical measuring apparatus makes it possible to measure the e.m.f. with a high accuracy. The slide wire is replaced with series of ten resistor coils forming "decades" that are connected in series to compensate for the e.m.f. being measured. The voltage drop in the accumulator circuit does not change. A sensitive mirror galvanometer is used as the null-instrument. The principle of com-

pensation measurement of the e.m.f. and of comparing the e.m.f. being measured with a standard cell is retained.

**19.5. Standard Cells.** The so-called *saturated Weston cell* is the basic standard cell used throughout the world.

The following electrode reactions proceed on the electrodes of a Weston cell:

on the left-hand electrode

$$Cd + SO_4^{2-},\ aq + \frac{8}{3} H_2O(lq) = CdSO_4 \cdot \frac{8}{3} H_2O(s) + 2e$$

on the right-hand electrode

$$Hg_2SO_4 + 2e = 2Hg(lq) + SO_4^{2-},\ aq$$

The right-hand half of the cell (Fig. 19.4) contains a paste of the solid salt $Hg_2SO_4$ in a saturated solution of $CdSO_4$ over a mercury electrode. The left-hand half contains an electrode consisting of 12.5% cadmium amalgam. The entire electrolyte is a saturated solution of $CdSO_4$ in equilibrium with the crystalline hydrate $CdSO_4 \cdot \frac{8}{3} H_2O$. The crystals of this salt fill the greater part of the vessel and ensure saturation of the solution when the temperature changes. The terminals are of platinum. The following reaction proceeds in a Weston cell:

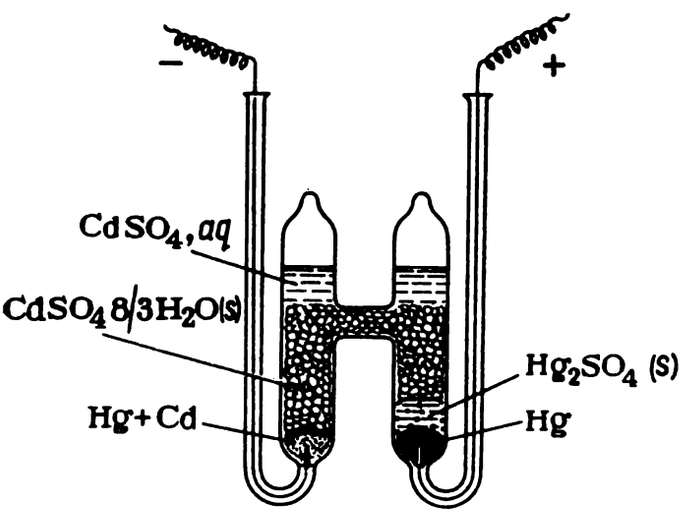



Fig. 19.4. Standard Weston cell

$$Cd + Hg_2SO_4(s) + \frac{8}{3} H_2O =$$
$$= 2Hg(lq) + CdSO_4 \cdot \frac{8}{3} H_2O(s)$$

The e.m.f. of a Weston cell has been determined by careful measurements at different temperatures. The e.m.f. of such a cell (in volts) prepared in accordance with the relevant rules, is expressed by the equation

$$E_t = 1.017\,964 - 0.0406 \times 10^{-3}\ (t - 20) -$$
$$- 9.5 \times 10^{-7}\ (t - 20)^2 + 10^{-8}\ (t - 20)^3$$

where $t$ is the temperature, °C. At 20 °C we have $E_{20\ °C} = 1.0180$ V. This equation is true within a temperature range from 0 to 40 °C. The temperature coefficient is small and averages —0.000 05 V/K.

The e.m.f.s of Weston cells prepared in various countries in accordance with international rules differ from the value indicated above by not more than 0.000 01 V.

An *unsaturated Weston cell* is also used as a standard one. It differs from the saturated cell in containing no solid cadmium sulphate. The solution of $CdSO_4$ in this cell is saturated with the solid salt at 4 °C, and is not saturated at higher temperatures. When the cell is thoroughly sealed, the concentration of the solution remains constant. The e.m.f. of this unsaturated Weston cell is equal to 1.0186 V. Its temperature coefficient is even smaller than for the basic Weston cell, and therefore this value of the e.m.f. does not practically change at room temperatures.

Previously the Clark cell

$$(-)Zn \mid ZnSO_4 + Hg_2SO_4(s) \mid Hg \mid Pt(+)$$

was also used as a standard one.

**19.6. Thermodynamics of Electrochemical Cells.** The electrical energy produced by a reversible elementary or complex cell is equal to the useful work $W'$ of the summary process proceeding in the cell, which we consider as a thermodynamic system. The useful work $W'$ of a reversible process is maximum and is equal to the decrease in the Gibbs energy of the system $-\Delta G$. This change in the Gibbs energy is caused by a complex of electrochemical reactions on the electrodes, i.e. by the total chemical reaction or other reversible physicochemical processes (solution, levelling out of the concentrations, phase transformation, etc.). When the process is a reversible one, it is possible, by making the cell function with almost complete compensation of its e.m.f. by an external potential difference, i.e. by making it be infinitely close to equilibrium (the measured value of $E$ corresponds to this process), to calculate the change in the Gibbs energy of the system $\Delta G$ through the measured e.m.f.[1]

With such compensation of the cell e.m.f. with the e.m.f. of the source of current, the total free energy change $\Delta G$ (and $E$) is equal to zero (equilibrium):

$$\Delta G = \Delta G_{cell} + \Delta G_{source} = 0$$

For $n$ gramme-equivalents of each of the participants of the process we have

$$\Delta G_{cell} = -\Delta G_{source} = -nFE \tag{19.1}$$

The derivative of $\Delta G_{cell}$ (in the following we shall use the symbol $\Delta G$ for purposes of brevity) with respect to the temperature

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -nF\left(\frac{\partial E}{\partial T}\right)_p = -\Delta S \tag{19.2}$$

Thus, having measured the e.m.f. of a cell and its temperature coefficient, we can easily find the quantities $\Delta G$ and $\Delta S$ for the

[1] Here the same abstract limiting case is used as for any reversible thermodynamic process, i.e. an infinitely slow one. The work of such a process is maximum.

total process in an electrochemical cell. This process is a spontaneous one, therefore $\Delta G < 0$.

An important thermodynamic characteristic of this process—the change in the enthalpy—is calculated by the Gibbs-Helmholtz equation [see Vol. 1, Sec. 4.3, Eqs. (4.18a) and (4.19a)].

$$\Delta G = \Delta H + T \frac{\partial}{\partial T} (\Delta G)_p$$

$$\Delta H = \Delta G - T \frac{\partial}{\partial T} (\Delta G)_p = -nFE + TnF \left( \frac{\partial E}{\partial T} \right)_p$$

*Example.* In the electrochemical cell

$$(-)\mathrm{Ag} \mid \mathrm{AgCl(s)} + \mathrm{HCl,\ aq} \mid \mathrm{Cl_2,\ Pt}(+)$$

the following electrochemical reactions proceed:

$$\mathrm{Ag(s)} + \mathrm{Cl^-} = \mathrm{AgCl(s)} + e$$

$$\frac{1}{2}\mathrm{Cl_2} + e = \mathrm{Cl^-}$$

Summation of these reactions gives the chemical reaction of formation of crystalline AgCl from silver and gaseous chlorine:

$$\mathrm{Ag(s)} + \frac{1}{2}\mathrm{Cl_2} = \mathrm{AgCl(s)}$$

The e.m.f. of this cell at 25 °C is 1.132 V, the temperature coefficient $(\partial E/\partial T)_p = -0.000\,477$ V/K. Using these values in the equations given above, we get for the reaction in question ($n = z = 1$)

$$\Delta G = -zFE = -1 \times 23\,062 \times 1.132 = -26\,100 \text{ cal}$$

$$\Delta S = zF \left( \frac{\partial E}{\partial T} \right)_p = -1 \times 23\,062 \times 0.000\,477 = -11.0 \text{ cal/K}$$

$$T\Delta S = -298 \times 11.0 = -3280 \text{ cal}$$

$$\Delta H = \Delta G + T\Delta S = -26\,100 - 3280 = -29\,380 \text{ cal}$$

The values of the changes in the thermodynamic functions obtained above allow us to directly find the values of the heats of formation of AgCl for two extreme cases (both at $p$ = const), namely:

1. A reversible process proceeding in an electrochemical cell at an infinitely small current intensity (an infinitely slow process):

$$Q_{\mathrm{rev}} = T\Delta S = -3280 \text{ cal}$$

2. A limiting irreversible process proceeding at a constant pressure and in the complete absence of useful work $W'$ (the direct interaction of silver and chlorine):

$$Q_{\mathrm{irrev}} = \Delta H = -29\,380 \text{ cal}$$

The quantity $Q_{rev}$ is equal to the heat liberated by a working electrochemical cell. It is possible in principle to measure the quantity $Q_{rev}$ as the absorbed heat if we place the cell in a calorimeter. But the value obtained will not be entirely accurate, since we cannot comply with the condition of the process proceeding at an infinitely slow rate. It is not difficult to calculate $Q_{rev}=T\Delta S$, however, knowing the e.m.f. at different temperatures, as was shown above in the example. The quantity $Q_{irrev}$ is the standard (tabulated) heat of formation of AgCl. It can be found directly or with the aid of Hess's law according to the results of calorimetric measurements.

The results of determining the quantity $Q_{irrev} = \Delta H$ by the electrochemical and calorimetric methods naturally coincide if the measurements are sufficiently reliable.

To characterize the separate types of electrochemical cells, their thermodynamic properties should be considered in greater detail. Let us relate the e.m.f. of a cell to the Gibbs energy and the equilibrium constant of the reaction proceeding in a cell in the same way as we have done this for electrode processes. Let a chemical reaction proceed in an operating electrochemical cell whose Gibbs energy is related to the equilibrium constant by the equation [see Vol. 1, Sec. 8.3, Eq. (8.19) and Sec. 8.7, Eq. (8.36)]

$$-\Delta G = RT \ln K_a - RT \sum_i \nu_i \ln a_i \tag{19.3}$$

Obviously

$$E = -\frac{\Delta G}{zF} = \frac{RT}{zF} \ln K_a - \frac{RT}{zF} \sum \nu_i \ln a_i \tag{19.4}$$

The first term in the right-hand part of Eq. (19.3) is constant at given values of $p$ and $T$. It may be designated by $E_0$. This is the standard e.m.f. of the cell, i.e. the e.m.f. at all $a_i = 1$, and for gas electrodes also at all $p_i = 1$. It is obvious that $E = 0$ when the activities and pressures of all the participants of the reaction are such that chemical equilibrium of the reaction sets in with the equilibrium constant $K_a$.

The equation makes it possible to compute the values of $\Delta G$ and $K_a$ according to the experimental values of $E$ and, conversely, compute the value of $E$ knowing the thermodynamic characteristics of a chemical reaction. Examples of the application of Eq. (19.4) will be considered in describing electrochemical cells of various types. Only solids and gaseous chlorine participate in the total reaction of formation of silver chloride in an electrochemical cell. Their thermodynamic state is unambiguously determined by the pressure and temperature. Very frequently solutes participate in the summary reaction (for example, in the Daniell-Jacobi cell). In such cases the Gibbs energy of the reaction depends not only on $p$ and $T$,

but also on the activities of the solutes, i.e. on the concentration of the solution. So that the activities of the solutes (see Sec. 22.1) can be calculated using the values of $E$ found experimentally.

Thus the measurement of the e.m.f. of an elementary or complex electrochemical cell is a simple and accurate method of calculating the thermodynamic characteristics of chemical reactions and some important physicochemical processes in solutions. This method can be used unconditionally only when the process of interest can be conducted reversibly in an electrochemical cell with division of the process into two parts corresponding to two reversible electrode processes.

CHAPTER 20

# ELECTRICAL POTENTIALS AT PHASE INTERFACES

**20.1. Appearance of Potential Jumps at Phase Interfaces.** When an electronic conductor comes into contact with an electrolyte, an *electrical double layer* forms at the electrode-solution interface. Let us consider a copper electrode immersed in a solution of $CuSO_4$ as an example. The chemical potential of the copper ions in the metal at a given temperature may be considered constant, while that in the solution depends on the concentration of the salt. Thus in the general case these chemical potentials are different. Let the concentration of the $CuSO_4$ be such that the chemical potential of the copper ions in the solution is greater than that in the metal. When the metal is immersed into the solution, part of the ions $Cu^{2+}$ dehydrate and pass over onto the metal, causing it to become positively charged. This charge will prevent the further migration of the ions $Cu^{2+}$ from the solution onto the metal and will result in the formation near the electrode of a layer of anions $SO_4^{2-}$ attracted to it (Fig. 20.1*a*). The so-called *electrochemical equilibrium* will set in, when the chemical potentials of the ions in the metal and in the solution will differ by the value of the potential difference of the electrical double layer formed:

$$2F\varphi = \mu_{Cu^{2+},s} - \mu_{Cu^{2+},m} \qquad (20.1)$$

where $\mu_{Cu^{2+},s}$ and $\mu_{Cu^{2+},m}$ are the chemical potentials of the copper ions in the solution and in the metal, respectively. The difference of the electrical potentials (for the ions $Cu^{2+}$) and the difference of the chemical potentials are compensated (at electrochemical equilibrium).

Let the concentration of the $CuSO_4$ be so small that the chemical potential of the copper ions in the solution is less than that in the metal. In this case the reverse process will occur when the metal is immersed in the solution. The copper ions will migrate from the electrically neutral crystal lattice of the metal into the solution, and the electrode will be charged negatively. This charge will prevent the further transition of the ions $Cu^{2+}$ into the solution, as a result of which new electrochemical equilibrium will set in. The structure of the electrical double layer in this case is shown schematically in Fig. 20.1*b*.

Such a concentration of the electrolyte ($c_0$) can obviously be selected at which the chemical potentials of the ions in the metal and in the solution are the same. Solutions with such a concentration are called *zero solutions*. When a metal is immersed into its zero solution no electrical double layer forms. As will be shown below, in this case, however, the potential difference between the metal and the solution is also not equal to zero.

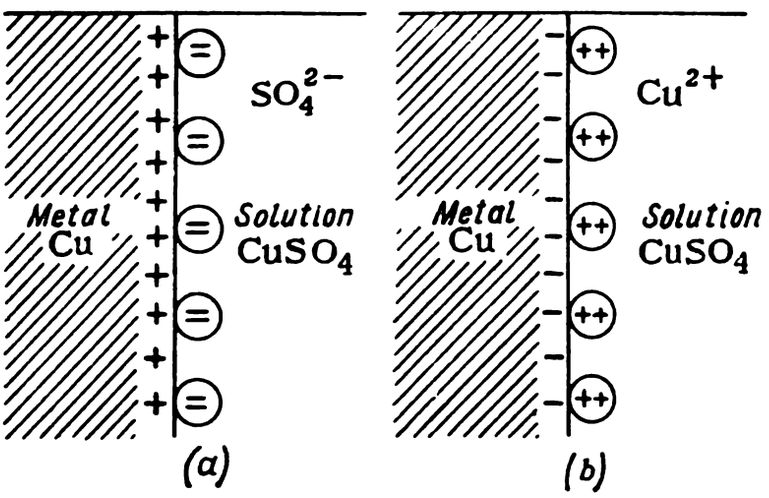



Fig. 20.1. Electrical double layer (two-dimensional model):
*a*—$\mu_{Cu^{2+},s} > \mu_{Cu^{2+},m}$; *b*—$\mu_{Cu^{2+},s} < \mu_{Cu^{2+},m}$

According to W. Nernst, the only source of the e.m.f. of an electrochemical cell is the electrical double layer on the surface of the electrodes. Thus, Nernst postulates that

$$E = \varphi_1 - \varphi_2 \tag{20.1a}$$

where $\varphi_1$ and $\varphi_2$ are the potential jumps in the ionic double layers. Nernst defines the potential of a metal in a zero solution as the absolute zero of potentials.

A. Frumkin showed that Nernst's conceptions are not true. Indeed, it was established on the basis of experimental data that the e.m.f. of an electrochemical cell consisting of two different electrodes immersed in their zero solutions differ from zero quite appreciably. For example, the potential difference between Pt and Cd in their zero solutions reaches 1.01 V. Therefore, the potential of an electrode in a zero solution, called the *zero-charge potential*, cannot be considered as the absolute zero of potentials.

For our further setting out of the material it is important to distinguish between two types of potential differences in a system consisting of several phases with interfaces between them. These may be electronic and electrolytic conductors, dielectrics and a vacuum.

The difference of the electrical potentials between two points in two different phases is called the *Galvani potential*. This may be

the potential difference at the surface of contact of a metal with another metal or a dielectric.

The *Volta* (or *contact*) *potential* is the potential difference between two points in a vacuum (or in a dielectric) near the surfaces of two metals (at a distance of the order of $10^{-5}$ to $10^{-4}$ centimetre from the surface of each metal). Since both points are in one phase, the Volta potential can be measured (see below).

As regards the potential difference between two points in different phases, i.e. the Galvani potentials, it is impossible to measure them, since electric charges are discrete and are always related to matter (ions, electrons). When a charged particle migrates from one phase to another, electrical work is always accompanied by work corresponding to the difference between the chemical potentials of the particle in the two phases. Only when the points are in a phase of constant composition is it possible to measure the potential difference between them, because the difference between the chemical potentials is equal to zero[1].

To understand the nature of the potential difference being measured between two electrodes immersed in their zero solutions, let us first consider the processes proceeding between plates of two different metals (for example, copper and zinc) separated by a vacuum. The electrons in a metal have kinetic energy at any temperatures (even at absolute zero). For this reason the electron gas leaves the limits of the crystal lattice of the metal and creates a certain pressure over it. A force of electrical attraction appears which balances the tendency of the electron gas to expand in the vacuum. In other words, an electrical double layer appears on the surface of the metal and, therefore, a potential jump. The magnitude of the latter depends on the nature of the metal and on the presence or absence on its surface of adsorbed molecules or atoms of impurities. The potential jump changes with a change in the work function of an electron, but these quantities are not equal.

This difference is due to the fact that in contrast to an imaginary charge, forces of a quantum nature act on an electron moving away from a metal (the so-called electrical mirror image forces), and also to the fact that an electron in a metal (in contrast to an imaginary charge) has a zero kinetic energy.

At points *a* and *b* (Fig. 20.2) definite, but different electrical potentials ($_1\varphi_0$ and $_2\varphi_0$) are produced in direct proximity to the surfaces of two metals *1* and *2* (for example, zinc and copper). As

[1] If the composition of an equilibrium phase continuously and regularly changes from point to point (for example, a column of a gas mixture in a gravitational field), the chemical potentials of the phase components undergo the corresponding continuous changes, which can be taken into account [see Vol. 1, Sec. 5.5, Eq. (5.14b)]. It is also possible to determine the difference of electrical potentials within the limits of such a phase.

a result when the zinc and copper are brought close to each other, the electrons begin to migrate from the surface of the zinc to that of the copper. This migration stops when the difference of potentials between points in the vacuum at the surface of the zinc and copper will be balanced by the difference between the work functions of the electrons in the two metals in a vacuum. Contact of the metals may only accelerate the migration of the electrons, but it can in no way change the appearing potential difference, since otherwise a perpetuum mobile would be obtained.

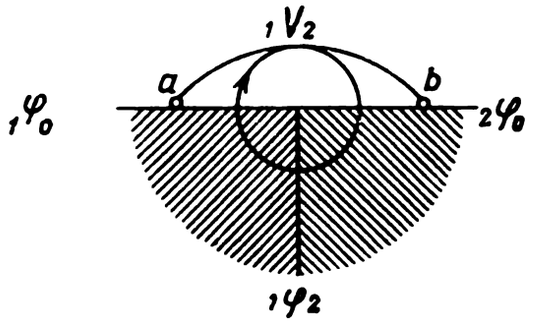



Fig. 20.2. Potential jumps at metal-metal and metal-vacuum interfaces

When electrostatic equilibrium sets in, let us mentally conduct an electric charge along the closed circuit in the direction shown by the arrow in Fig. 20.2. Returning to the initial point, we should get the value of the potential at this point. Therefore

$$_1V_2 = {}_1\varphi_2 - {}_1\varphi_0 + {}_2\varphi_0 \qquad (20.2)$$

Let us conduct an experiment that will help us to measure the value of the Volta potential. Connect plates of two different metals in an atmosphere of an inert gas to a voltmeter having a very high resistance (an electronic voltmeter or electrometer).

As indicated above, an electric field appears in the space between the metals. Its value is determined by the Volta potential of the two metals. If we ionize the gas between the metals, for instance with the aid of radioactive radiation, the ions of the gas under the action of the field will come into motion. They will discharge on the plates and give up their charge to them until the initial potential difference, i.e. the Volta potential, will be compensated. The voltmeter will show a potential difference equal in value and opposite in sign to the Volta potential.

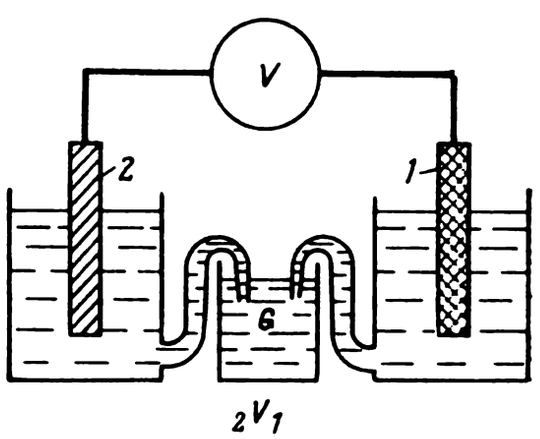



Fig. 20.3. Cell consisting of two metals (*1* and *2*) in zero solutions

Thus the e.m.f. of a circuit consisting of two different metals separated by an ionized gas is equal to their Volta potential $_1V_2$.

A similar result is obtained when we consider the e.m.f. of a cell consisting of two different metals immersed in their corresponding zero solutions (Fig. 20.3). Let the conductors connected to the volt-

meter be made of metal *1* or *2*. The circuit closed through the voltmeter has the contacts water-*2*, *2-1* and *1*-water.

The ionic double layers on the metal-solution interface are absent, since zero solutions are taken. The diffusion (liquid junction) potential at the boundary between the two liquids has been eliminated owing to the use of a salt bridge with a saturated solution of potassium chloride in intermediate glass *G* (see Sec. 21.3). Here also it is the Volta potential that is measured, but in water (considered as a dielectric) instead of a vacuum. Thus in this case

$$_1V_2 = {}_1\varphi_2 - {}_1\varphi_{\text{water}} + {}_2\varphi_{\text{water}} \tag{20.2a}$$

It is obvious that $_1\varphi_0 \neq {}_1\varphi_{\text{water}}$ owing to adsorption of the water dipoles and the influence of adsorption on the electron double layer on the surface of the metal. If we assume that the adsorption of water molecules on different metals results in the same (in the first approximation) change in the potential jumps on these metals, then their Galvani potentials in the liquid dielectric $_1\varphi_{\text{water}}$ and $_2\varphi_{\text{water}}$ differ by the same value from the Galvani potentials $_1\varphi_0$ and $_2\varphi_0$ in a vacuum. Thus

$$_1\varphi_0 - {}_2\varphi_0 \approx {}_1\varphi_{\text{water}} - {}_2\varphi_{\text{water}} \tag{20.3}$$

and therefore the potential difference $_1V_2$ being measured between the two different metals in their zero solutions, i.e. the difference between their zero-charge potentials, is approximately equal by Eqs. (20.2) and (20.3) to the contact difference of potentials of these two metals in a vacuum (the Volta potential between them). This conclusion, first made by Frumkin, was confirmed experimentally. Thus, the Volta potential between two metals in a vacuum is equal to —0.36 V for liquid bismuth and thallium; the difference between the zero-charge potentials of these metals is equal to —0.35 V. The corresponding values for liquid tin and thallium are —0.46 and —0.42 V.

If the metals are immersed in solutions other than zero ones, ionic double layers also appear at the electrode-solution interfaces. Thus the measured e.m.f. of an electrochemical cell with two electrodes and without diffusion potentials between the liquid solutions consists of the contact (Volta) potential of the metals in water (considered as an insulator) and the potential differences in the ionic double layers $\varphi_1$ and $\varphi_2$ appearing as a result of the exchange of ions between the metals and the solution:

$$E = \varphi_1 - \varphi_2 + {}_1V_2 \tag{20.4}$$

The ionic double layers on the electrodes are always of such a nature that the e.m.f. of an electrochemical cell corresponds to the total process in this cell. For example, the adsorption of polar molecules

on electrodes changes the contact potential ${}_1V_2$ between the electrodes. But the potentials $\varphi_1$ and $\varphi_2$ of the ionic layer on the electrodes also change, so that the e.m.f. remains the same as in the absence of adsorption of the molecules on the electrodes. In studying the thermodynamics of electrochemical processes, it is sufficient to know that the change in the energy of an electrochemical cell is completely determined by the chemical reactions on the electrodes. In studying the kinetic laws, however, it is also necessary to know the mechanism of the electrode processes. Changes in the structure of the electrical double layer on electrodes, which do not affect the equilibrium values of the electrode potentials, do affect the rates of the electrochemical reactions. For this reason in studying the kinetics of electrode processes it is very important to know the zero-charge potentials, and also the molecular structure of the electrode-solution interface.

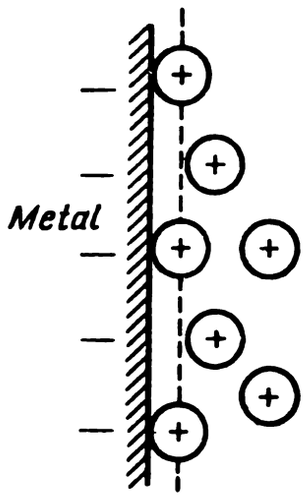



Fig. 20.4. Distribution of cations in electrical double layer

**20.2. Structure of Electrode-Solution Interface.** As already noted, an electrical double layer forms at the interface between an electronic-conductor and an electrolyte. However, the double layer considered above (see Fig. 20.1), which forms a plane capacitor on a flat electrode, is only a simplified model. Such a model was first proposed by H. Helmholtz in 1879. Later investigations showed that the ions of the electrical double layer participate in thermal motion, which causes to some extent the diffusion of the double layer. Thus the Helmholtz model would correspond to actual conditions if the temperature of the system were equal to absolute zero, i.e. if there were no thermal motion. In actual conditions with elevation of the temperature part of the ions migrate from the surface of the electrode into the so-called diffuse part of the double layer (sometimes called the Gouy layer), and the other part remains on the surface of the electrode (see Fig. 20.4). The region between the diffuse part of the double layer and the surface of the metal is called the *fixed part of the electrical double layer*, or the *Helmholtz layer*. The latter is shown

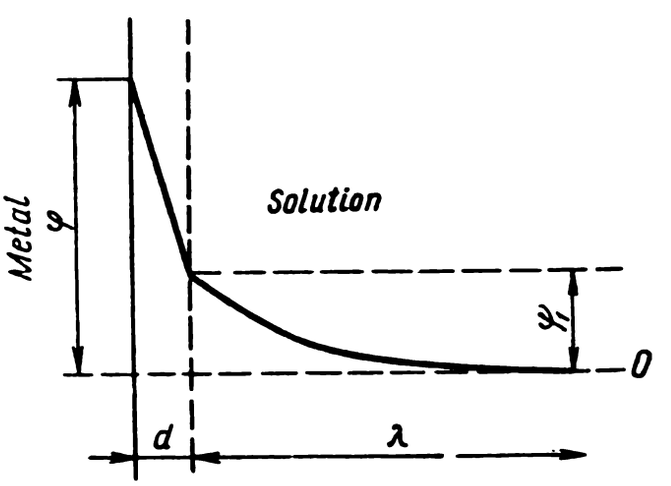



Fig. 20.5. Distribution of potential in electrical double layer

by a dotted line in Fig. 20.4. The distribution of the potential in the electrical double layer in the absence of specific (i.e. non-electrostatic) adsorption is shown schematically in Fig. 20.5.

Since there are no electric charges inside the fixed part of the double layer, the potential here changes linearly with a growth in the distance from the electrode (see Fig. 20.5, region *d*). At the same time in the diffuse part of the double layer (region λ), as shown by calculations, the potential changes according to an exponential law. The total potential $_{Me}\psi_{sol}$ can be represented in the form of two addends, namely, the potential of the diffuse part of the double layer $\psi_1$ and that of the fixed part of the double layer $_{Me}\psi_{sol} - \psi_1$. The thickness of the fixed part (*d*) is approximately equal to the radius of the ions forming the layer, while the thickness of the diffuse part (λ), which is similar to an ionic atmosphere, is determined at a given temperature by the charge and concentration of the ions in this part. Thus the thickness of the diffuse part of the double layer in very dilute solutions reaches several thousands of angstroms, while in concentrated ones it decreases to tens and even several angstroms. The structure of the electrical double layer in this case approaches the Helmholtz model.

When great specific adsorption of ions takes place under the action of chemical or van der Waals forces, for example the adsorption of anions on the surface of a mercury electrode, the total charge of the ions in the fixed part of the double layer may be greater than the charge of the electrode surface. This phenomenon is called *recharging of the surface*. In this case the potential at a distance from the surface of the electrode equal to an ion radius (the $\psi_1$-potential) has a sign opposite to that of the difference of potentials between the electrode and the solution. The distribution of the potential in the electrical double layer in this case is shown schematically in Fig. 20.6.

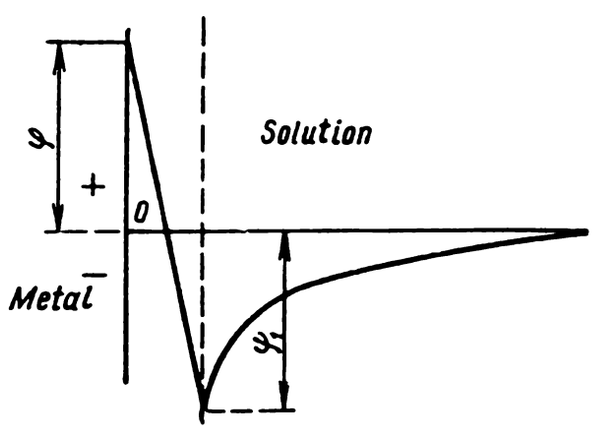



Fig. 20.6. Distribution of potential in recharging of surface owing to great specific adsorption of anions

**20.3*. Methods for Determining Zero-Charge Potentials.** The capacitance of a capacitor relates its charge to the potential difference between its plates. We consider the electrical double layer on the surface of an electrode as a capacitor and relate the capacitance of the double layer and its charge to one square centimetre of the electrode surface. Hence the relation between the specific capacitance of the double layer *C*, its surface charge density σ and the potential jump φ can be written as

$$C = \frac{\sigma}{\varphi}$$

In the following we shall call the specific capacitance *C* of the double layer simply its capacitance.

One of the methods for determining the zero-charge potential is based on measurement of the capacitance of the electrical double layer. In the absence of specific adsorption, the capacitance of the electrical double layer is equal to that of two capacitors connected in series, of which one is equivalent to the fixed part (Helmholtz layer), and the other to the diffuse part of the double layer. From the formula for the capacitance of series-connected capacitors we get

$$\frac{1}{C}=\frac{1}{C_H}+\frac{1}{C_d} \tag{20.5}$$

where $C$ = capacitance of electrical double layer
$C_H$ = capacitance of Helmholtz layer
$C_d$ = capacitance of diffuse part of double layer.

Equation (20.5) can be rewritten as

$$C=\frac{C_H C_d}{C_H+C_d} \tag{20.6}$$

A glance at Eq. (20.6) shows that the smaller of the quantities $C_H$ and $C_d$ predominates in determining the total capacitance of the electrical double layer. The capacitance of the Helmholtz layer is determined by the dimensions of the adsorbed ions and their ability to deform under the action of an electric field. For this reason at a constant temperature $C_H$ is a function only of the charge of the surface and does not depend on the concentration of the electrolyte. The values of the capacitance of the Helmholtz layer usually range from 20 to 40 $\mu F/cm^2$. In contrast to $C_H$, the capacitance of the diffuse part of the double layer appreciably depends on the concentration of the electrolyte (it decreases with greater dilution, and also with lowering of the electrode charge). If the concentration of the electrolyte is high, the capacitance of the diffuse part of the double layer considerably exceeds that of the Helmholtz layer, and $C \approx C_H$ [see Eq. (20.6)]. In sufficiently dilute solutions (0.01 $N$ and less), however, at low charges of the electrode (i.e. near the zero-charge potential) the capacitance of the diffuse part becomes less than that of the Helmholtz layer and determines the total capacitance of the electrical double layer. Thus a minimum is observed on the curve showing how the capacitance of the double layer depends on the potential of the electrode for dilute solutions. The position of this minimum allows us to determine the zero-charge potential of the electrode.

For a liquid metal (for example, mercury), the zero-charge potential of an electrode can be determined by measuring the dependence of the interface tension on the potential of the electrode. Indeed, in the formation of a double layer, the electric charges of the metal surface (their sign does not matter) mutually repel each other, which causes a decrease in the interface surface tension $\gamma$ of the metal. By changing the potential $\varphi$ imparted to the metal (relative to the other electrode), the charge density of the double layer and the interface tension of the metal are changed. Figure 20.7 shows the dependence of the interface tension $\gamma$ of mercury on the potential, the so-called *electrocapillary curve*.

The Lippmann thermodynamic equation relates the derivative of the function $\gamma = f(\varphi)$ describing the electrocapillary curve to the surface charge density o:

$$\frac{\partial\gamma}{\partial\varphi}=-\sigma \tag{20.7}$$

Obviously, at the maximum point of the curve $\sigma = 0$ and, therefore, the potential of the metal corresponding to the maximum of the electrocapillary curve is the zero-charge potential.

It was found experimentally that depending on the composition of a solution and especially on the presence of substances which are adsorbed on the surface of mercury, the potential of the electrocapillary maximum and, consequently.

the zero-charge potential changes (Fig. 20.8). In addition, the zero-charge potentials also differ for different metals and, consequently, as already indicated, cannot serve as the "absolute zero of potentials". Thus, the potential of the electrocapillary maximum for mercury is equal to — 0.20 V, for gallium to —0.66 V and for cadmium to —0.9 V (relative to the standard hydrogen electrode).

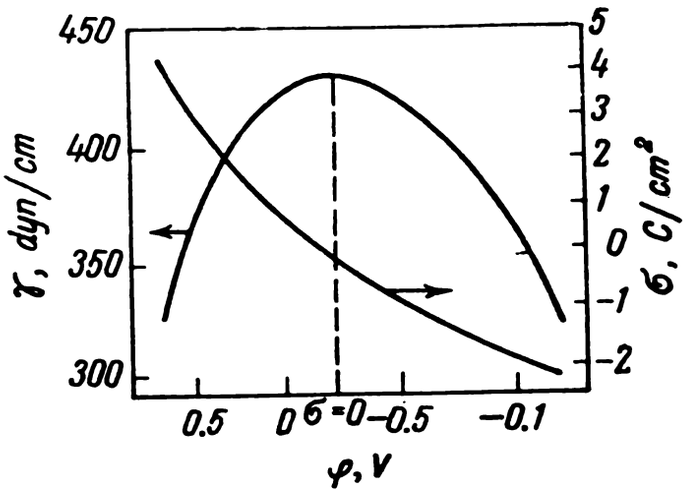



Fig. 20.7. Dependence of interface surface tension and charge of mercury surface on potential

The dependence of the zero-charge potential on the composition of the electrolyte is explained by the adsorption of ions and polar molecules on the surface of the electrode. This leads to the formation of an electrical double layer and the appearance of a potential jump inside the electrolyte near the surface of the metal (Fig. 20.9). Figure 20.9*a* schematically shows the adsorption of $I^-$ anions from a solution containing KI on the surface of a metal having a zero-charge potential. The attraction of the potassium ions to the layer of adsorbed ions leads to the formation of an electrical double layer at the surface of the metal inside the solution and, consequently, to the appearance of a potential jump. Figure 20.9*b* shows a similar phenomenon in the adsorption of polar molecules of butyl alcohol.

The zero-charge potential of a liquid metal can also be determined with the aid of an open dropping (mercury) electrode (see Sec. 24.12).

Electrocapillary phenomena were used by G. Lippmann in designing a capillary electrometer that can serve as an instrument showing the absence of a current, i.e. a zero potential difference in a circuit.

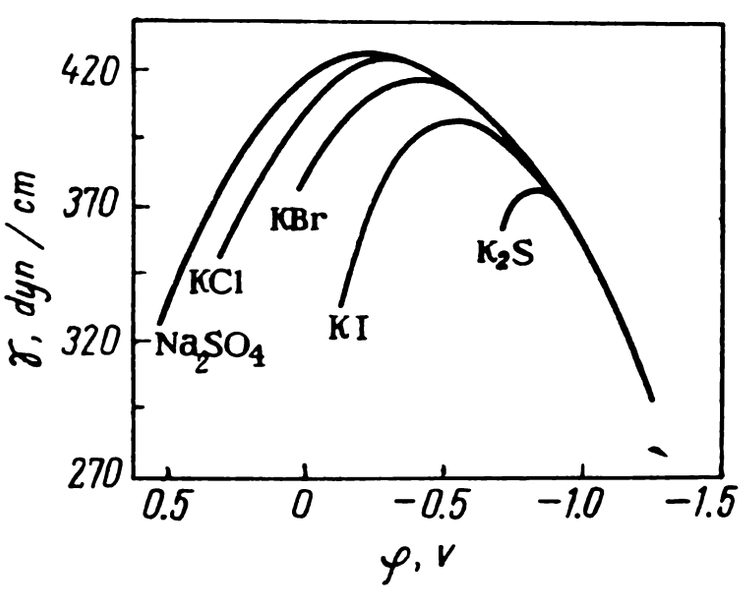



Fig. 20.8. Influence of anion adsorption on shape of electrocapillary curve

Figure 20.10 shows a Lippmann-Quincke capillary electrometer. The mercury in capillary *B* is under a solution of $H_2SO_4$. The surface of the mercury is charged positively relative to the solution, its potential is $\varphi$ and surface tension $\sigma_0$. When a current flows from capillary *B* to *C*, the positive charge of the mercury surface decreases, its surface tension gradually grows to $\sigma$, and the level of the mercury in capillary *B* drops.

If the potential difference between *C* and *B* is made to equal zero by compensation, then when the circuit is connected there is no current and the level of the surface of the mercury in capillary *B* remains stationary. The capillary electrometer designed by G. Gouy (Fig. 20.11) is used to study experimentally how the surface tension at the liquid metal-solution interface depends on the potential difference. The instrument allows us to measure the

pressure of mercury column $l$ essential for the mercury meniscus to be at a definite distance from the end of tapered capillary $a$ at a given potential jump of

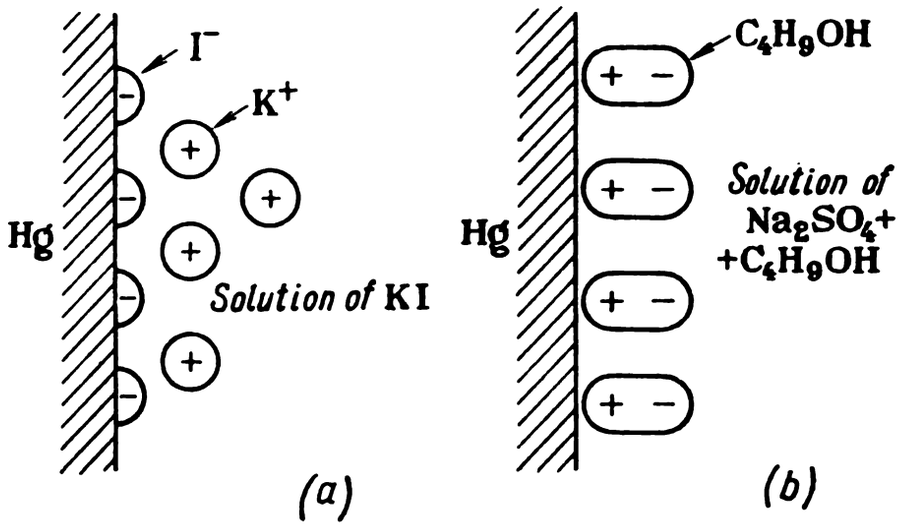



Fig. 20.9. Electrical double layer at surface of metal having zero-charge potential:

*a*—adsorption of iodide ions; *b*—adsorption of polar molecules

the mercury (measured relative to auxiliary electrode $c$). If the capillary is completely wetted by the solution, the height $l$ of the mercury column is proportional to the surface tension of the mercury relative to the solution. The electrometer is also provided with rheostat $d$ and level balancer $e$.

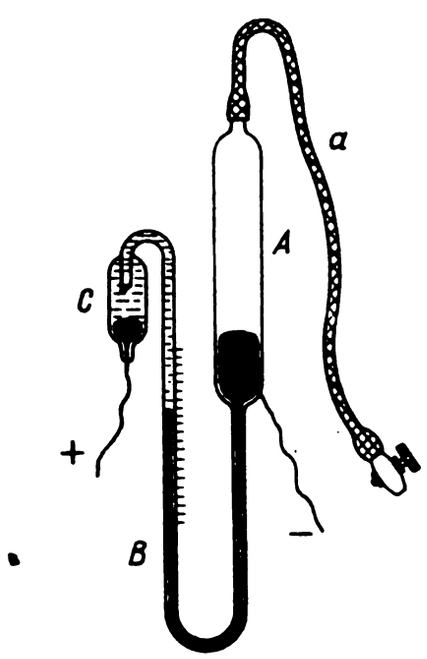



Fig. 20.10. Lippmann-Quincke capillary electrometer

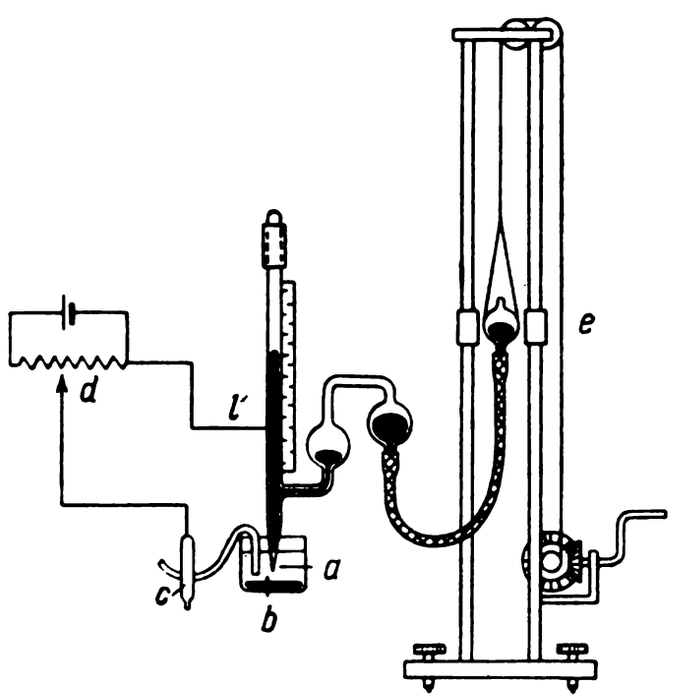



Fig. 20.11. Gouy capillary electrometer

**20.4. Magnitude and Sign of Electrode Potential.** Like the difference of potentials between two points in different phases, it is impossible to measure experimentally the potential jump at the

electrode-solution interface. The magnitude of such a potential jump can be calculated theoretically, but only if we know exactly the structure of the interface between the two phases. At present the structure of the interface between an electrode and a solution has been studied insufficiently. Therefore the question as to how the e.m.f. of a galvanic cell is composed of the separate potential jumps at the phase interfaces (i.e. the problem of the absolute potential) remains open.

Since it is possible to measure only the e.m.f. of an electrochemical cell, we can find experimentally only the relative magnitudes of the so-called *electrode potentials*, i.e. the e.m.f. of a cell formed from a given electrode and a certain *standard* electrode whose potential is conventionally taken equal to zero. Such a standard or *reference electrode* is the reversible hydrogen electrode, in which gaseous hydrogen is under a pressure of one atmosphere and saturates a platinum electrode. The solution into which the hydrogen electrode is immersed contains hydrogen ions (hydroxonium), the activity of $H^+$ being equal to unity.

The values of the activity of separate species of ions cannot be determined by thermodynamic methods (see Sec. 16.4). The same can be said about the potential jump on a separate electrode. Actual measurements of the e.m.f. are conducted for a combination of at least two electrodes reversible relative to a certain ion. The condition for the standard states of these electrodes is considered to be $a_+ = 1$ or $a_- = 1$. Hence the actual standard state for the e.m.f. of cells is determined by the equality to unity of the mean ionic activity of a dissociating compound.

The *electrode potential* is the e.m.f. of a cell consisting of this electrode (on the right) and a standard hydrogen electrode (on the left). For example, to find the electrode potential of zinc the following cell is formed:

$$(+)\mathrm{Pt},\ H_2 \mid H^+,\ aq \parallel Zn^{2+},\ aq \mid Zn(-)$$

The e.m.f. of this cell is negative, since the positively charged electrode is on the left (see Sec. 19.3). If the activity of the $Zn^{2+}$ in the solution is equal to unity, the e.m.f. of the cell is equal to —0.763 V. This is the standard electrode potential of zinc. To find the electrode potential of copper the following cell must be formed:

$$(-)\mathrm{Pt},\ H_2 \mid H^+,\ aq \parallel Cu^{2+},\ aq \mid Cu(+)$$

Here the e.m.f. and, therefore, the standard electrode potential of the copper are equal to +0.337 V. In the representation of a half-cell it is good to write the combination electrode + ion in solution in the sequence used to show a cell consisting of a standard hydrogen electrode and the given one. The electrode potential should be given with the corresponding sign for an electrode written in this way. For

example

$$\begin{array}{ll} Zn^{2+},\ aq\,|\,Zn; & \varphi = -0.763\ V \\ Cu^{2+},\ aq\,|\,Cu; & \varphi = +0.337\ V \end{array} \qquad (A)$$

The sign "plus" corresponds to motion of the ions from the left to the right (from the solution to the electrode in a cell where the electrode being considered is connected to a hydrogen electrode). Obviously, when the reverse order is used for writing, the sign of the potential should be changed:

$$\begin{array}{ll} Zn\,|\,Zn^{2+},\ aq; & \varphi = +0.763\ V \\ Cu\,|\,Cu^{2+},\ aq; & \varphi = -0.337\ V \end{array} \qquad (B)$$

Only the first way of writing (A) leads to the signs of the quantities $\varphi$ that correspond to the electrode potentials. The quantities corresponding to the way of writing shown in (B) should never be called electrode potentials. But representations (A) and (B) can be used in calculating the e.m.f. of an elementary or complex cell. If in writing a cell, an electrode is arranged in the same way as in its combination with a hydrogen electrode in accordance with the rule for determining the electrode potential given above, the magnitude of the electrode potential is taken from tables of standard potentials with the sign given.

For $Zn^{2+}$, aq | Zn the value of $\varphi = -0.763$ V will enter into the total e.m.f.

For $Cu^{2+}$, aq | Cu we have $\varphi = +0.337$ V.

If an electrode is written in a cell in the reverse position, the tabulated value with the reverse sign will enter into the sum. For example

$$\begin{array}{lll} (-)Zn\,|\,Zn^{2+},\ aq\,||\,Cu^{2+}, & aq\,|\,Cu(+) \\ +0.763\ V & +0.337\ V \end{array}$$

$$E = 0.763 + 0.337 = 1.110\ V$$

The diffusion potential occurring at the interface of the solutions $CuSO_4$ || $ZnSO_4$ makes the calculation more complicated (see Sec. 21.3).

As regards the Galvani potentials between different electronic conductors (metals), they cannot be eliminated.

As previously indicated, the material of the connecting wires does not affect the e.m.f. of a cell. But since the platinum-hydrogen electrode is the standard one, the Galvani potential Pt | Me is always present. It is a component of the electrode potential of the given electrode. Thus the electrode potential $Me^{n+}$ | Me measured relative to the hydrogen electrode is actually the sum of three Galvani potentials

$$Me^{n+}\,|\,Me + Me\,|\,Pt + Pt\,|\ \text{solution}$$

At a given temperature the Galvani potentials Me | Pt and Pt | solution are constant. For this reason in investigating how the electrode potential depends

on the composition and concentration of a solution, we study this dependence for the potential at the interface $Me^{n+}$ | Me. When a cell is formed of two electrodes ($Me_1$ and $Me_2$), the difference between the Galvani potentials $Me_1$ | Pt and $Me_2$ | Pt is obviously equal to the Galvani potential $Me_2$ | $Me_1$. The latter is one of the addends of the cell e.m.f. The value of the e.m.f. calculated as the difference between the electrode potentials coincides with experimental data.

On the other hand, the electrode potential $Me^{n+}$ | Me can be represented as the sum of the potential jumps in the electrical double layers at the given and hydrogen electrodes and the Volta potential between this metal and the zero hydrogen electrode.

The e.m.f. of a cell formed of two metal electrodes can obviously be represented as the sum of the Volta potential between the two electrodes (in water) and the potential jumps of the electrical double layers on these electrodes.

**20.5. Dependence of Electrode Potential on Concentration of Solution.** The dependence of the electrode potential on the concentration (activity) of a substance in an electrolyte participating in an electrochemical reaction can be established by methods of thermodynamics. The following electrochemical reaction proceeds on an electrode $Me^+$ | Me with an equilibrium potential $\varphi$:

$$Me^+, aq + e = Me$$

Since the ions of the metal in the crystal lattice are also charged positively, and the "free" electrons of the metal are bound to the lattice before and after the process, it is more correct to write

$$Me^+nH_2O \text{ (in solution)} \rightarrow Me^+ \text{ (in crystal)} + nH_2O$$

This is a reaction of dehydration of the metal ion and its inclusion into the crystal lattice.

For an equilibrium process at constant $T$ and $p$, the decrease in the Gibbs energy ($-\Delta G$) is equal to the maximum work $W'$ [see Vol. 1, Sec. 4.2, Eq. (4.14)]. The work $W'$ per gramme-ion of $Me^+$ of an electrochemical cell is equal to the work done by the electric current $zF\varphi$ [Eq. (19.1)]

$$W' = -\Delta G = zF\varphi \tag{20.8}$$

When one gramme-ion of the metal migrates from the solution onto the electrode, the change in the Gibbs energy is equal to the difference between the chemical potentials of the substance in two pha es, namely, in the solution ($\mu'$) and in the electrode ($\mu''$)

$$\Delta G = \mu''_+ - \mu'_+ \tag{20.9}$$

At constant pressure and temperature in an electrode of a constant composition (pure metal)

$$\mu''_+ = \mu^\circ_+ = \text{const} \tag{20.10}$$

In a solution, in accordance with Eq. (16.7)

$$\mu'_+ = \mu'^{\circ}_+ + RT \ln a_+ \tag{20.11}$$

Here $\mu_+^{\prime\prime\circ}$ is the chemical potential of an ion in the solution in the standard state. This quantity is constant at a given temperature. Thus

$$\Delta G = \mu_+^\circ - \mu_+^{\prime\prime\circ} - RT \ln a_+ \tag{20.12}$$

Comparing Eqs. (20.8) and (20.9), we get

$$\varphi = -\frac{\mu_+^\circ - \mu_+^{\prime\prime\circ}}{zF} + \frac{RT}{zF} \ln a_+ \tag{20.13}$$

The first term of the right-hand part of Eq. (20.13) is a constant quantity at constant pressure and temperature (for a metal electrode this quantity is practically independent of the pressure). This term can be denoted by the symbol $\varphi^\circ$:

$$\varphi = \varphi^\circ + \frac{RT}{zF} \ln a_+ \tag{20.14}$$

For a dilute solution we may use the concentrations instead of the activities ($a_+ \to m_+$, $c_+$, $x_+$) depending on the measure of the concentration selected and the corresponding standard state for the activity. Using the molality $m$, as is usual practice for electrolytes, we get for a dilute solution

$$\varphi = \varphi^\circ + \frac{RT}{zF} \ln m_+ \tag{20.15}$$

It is quite obvious that $\varphi^\circ$ is the potential of an electrode relative to a solution where the corresponding ions have an activity equal to unity ($a_+ = 1$). The quantity $\varphi^\circ$ is called the *standard electrode potential*. It depends on the temperature.

Equation (20.15) was derived in 1888 by W. Nernst in a different way. This equation, and also the more general equation (20.14), is called the *Nernst equation for the electrode potential*.

To find $\varphi^\circ$ it is necessary to use Eq. (20.14), introducing $a_+ = \gamma_+' m_+$ and solving it with respect to $\varphi^\circ$:

$$\varphi^\circ = \left(\varphi - \frac{RT}{zF} \ln m_+'\right) - \frac{RT}{zF} \ln \gamma_+' \tag{20.16}$$

Reducing $m_+$ (the concentration of the corresponding salt), we can find the limit to which the quantity in parentheses tends when $m \to 0$ and, therefore, $\gamma_+' \to 1$.

$$\varphi^\circ = \lim \left(\varphi - \frac{RT}{zF} \ln m_+\right) \text{ when } m \to 0 \tag{20.17}$$

The above deduction is a simplified one, and Eq. (20.17) has an essential shortcoming. The matter is that not only a cation (or an anion for such electrodes as the iodine or chlorine ones, see Sec. 20.7) participates in an electrode process as a whole, but also always an ion of the opposite sign, for example an anion, $t_-$ gramme-equivalents of which simultaneously with the migration of Me onto the electrode (process 1) left the solution surrounding the electrode. This solution

was entered by $t_+$ gramme-equivalents of cations. In addition, what is always measured is the e.m.f. of a cell, and not the absolute value of the electrode potential, and for this reason the measured value of $E$ corresponds to the summary process in the cell.

Ions of both signs participate in all chemical processes in cells. This is why it is impossible to determine the activity of ions of one sign, $a_+$ or $a_-$, from the measurements of the e.m.f. As a result the mean ionic activity $a_\pm$ is obtained (in known conditions). It is possible to determine all the changes undergone by the dissolved salts, i.e. simultaneously by the cations and anions, only for the chemical process in a cell as a whole, and to compare the measured values of $E$ with the changes in the chemical potentials $\mu_\pm$, activities $a_\pm$ and molalities $m_\pm$ of the dissolved salts. Somewhat later we shall consider several examples. Meanwhile we shall assume that for simple electrolytes (one salt is dissolved) the activity coefficient of a cation is by convention equal to the mean activity coefficient of the salt.

Considering that $\gamma'_\pm \approx \gamma'_+$ and $m_+ \approx m_\pm$, for a binary mono-monovalent electrolyte ($z = 1$) we have

$$\varphi = \varphi^\circ + \frac{RT}{F} \ln a_\pm = \varphi^\circ + \frac{RT}{F} \ln m_\pm + \frac{RT}{F} \ln \gamma'_\pm \qquad (20.18)$$

Inserting $F = 23\,062$ cal/g-eq·V and the coefficient for transition from natural to common logarithms (2.3026), we get for $z = 1$

$$\varphi = \varphi^\circ + 0.0577 \log m_\pm \gamma'_\pm \quad (T = 291 \text{ K}) \qquad (20.19)$$

$$\varphi = \varphi^\circ + 0.0591 \log m_\pm \gamma'_\pm \quad (T = 298 \text{ K}) \qquad (20.20)$$

If we have an electrolyte $M_pA_q$ whose ion participates in the electrode process, then

$$a_\pm = (a_+^p a_-^q)^{\frac{1}{p+q}} \qquad (20.21)$$

if $a_+ = a_-$, i.e. $p = q$ and $z_+ = z_- = z$, then

$$\varphi = \varphi^\circ + \frac{0.0577}{z} \log a_\pm \qquad (20.22)$$

**20.6. Reference Electrodes.** The basic reference electrode is the standard hydrogen electrode (SHE)

$$\begin{array}{c|c} \text{Pt, } H_2 & H^+A^- \\ (p_{H_2}=1 \text{ atm}) & (a_+ = 1) \end{array}$$

for which it is conventionally assumed that $\varphi^\circ = 0$.

A hydrogen electrode is a platinized[1] platinum plate in a solution containing hydrogen ions (usually a solution of $H_2SO_4$ or HCl). A flow of pure hydrogen under a constant pressure is passed through the solution. The solution is placed in special vessels which may have different shapes (see Fig. 20.12). The electrode should be only partly immersed in the solution.

[1] The plate is platinized to increase the active surface of the electrode, which facilitates the transition of the adsorbed hydrogen from the electrode into the solution and the reverse transition of the hydrogen from the solution.

The following equilibria exist in a hydrogen electrode:

$$H_2(\text{gas}) \rightleftarrows 2H \text{ (adsorbed by platinum)} \underset{}{\overset{+2H_2O}{\rightleftarrows}} \Big|^{\varphi} \rightleftarrows 2H_3O^+ + 2e$$

Since the hydrogen adsorbed by the platinum is in equilibrium with the gaseous hydrogen, we can consider electrochemical equilibrium and omit the intermediate step:

$$H_2\ (\text{gas}) \overset{+2H_2O}{\rightleftarrows} \Big|^{\varphi} \rightleftarrows 2H_3O^+ + 2e$$

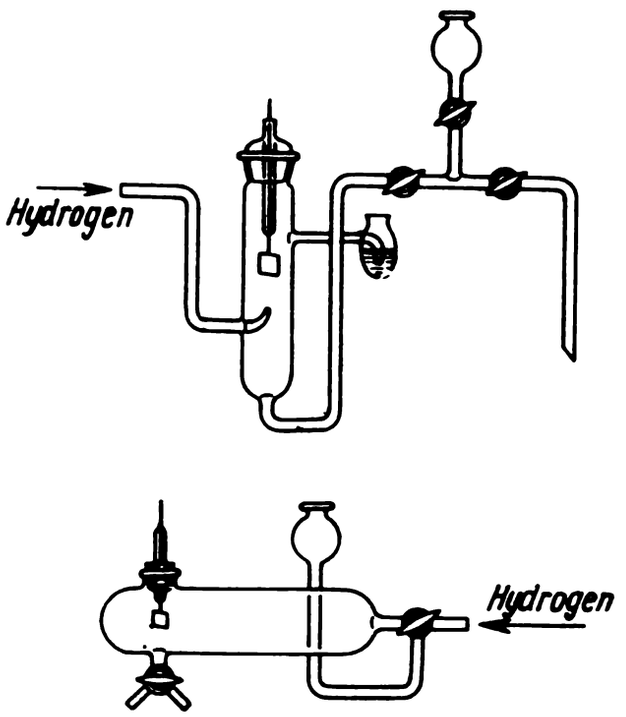



Fig. 20.12. Hydrogen electrodes

The electrode potential of a nonstandard hydrogen electrode, not equal to zero, depends on the pressure of the hydrogen and the activity of the solution

$$\begin{array}{l|l} \text{Pt, } H_2 & H^+A^- \\ (p_{H_2} \gtrless 1) & (a_\pm \lessgtr 1) \end{array}$$

Here for $H_2$ (an ideal gas) on the electrode ($\mu''$) and for $H^+$ in the solution ($\mu'$) we have

$$\mu'' = \mu''^{,\circ} + RT \ln p$$

and

$$\mu' = \mu'^{,\circ} + RT \ln a_+$$

Repeating for the reaction $H^+ \rightarrow \frac{1}{2}H_2$ the reasoning set out above (pp. 513-514), we get

$$\Delta G = \frac{1}{2}\mu'' - \mu' = \left(\frac{1}{2}\mu''^{,\circ} - \mu'^{,\circ}\right) + RT \ln p^{1/2} - RT \ln a_+$$

$$\varphi = -\frac{0.5\mu''^{,\circ} - \mu'^{,\circ}}{F} + \frac{RT}{F} \ln \frac{a_+}{p^{1/2}} = \frac{RT}{F} \ln \frac{a_+}{p^{1/2}} \qquad (20.23)$$

The first term in the sum of Eq. (20.23) is equal to zero according to the initial condition. Thus the potential of a hydrogen electrode decreases with an increase in the pressure of the hydrogen on the electrode. The deviation of the pressure from the normal value by 0.1 atm results in a change in the potential $\varphi$ by 0.0012 V. In accurate measurements a correction should be introduced for the pressure of the hydrogen (with account of the saturated vapour pressure of the solution).

Work with a hydrogen electrode requires that a number of precautions be strictly observed. It is much simpler to work with a *calomel electrode*, which may serve as an auxiliary reference electrode,

since it is easy to prepare it and its potential relative to a hydrogen electrode is known exactly. A calomel electrode (it would be more proper to call it a mercury-calomel electrode) consists of a mercury electrode in a solution of KCl of a definite concentration saturated with $Hg_2Cl_2$ (calomel)

The potential of the mercury electrode is related to the concentration of the mercury salt in the solution by an equation of the type of Eq. (20.14)

$$\varphi_{Hg} = \overset{\circ}{\varphi}_{Hg} + \frac{RT}{2F} \ln a_{Hg_2^{2+}}$$

In a saturated solution of $Hg_2Cl_2$ the product of the activities of the ions $a_{Hg_2^{2+}} a^2_{Cl^-} = K_{ap}$ is a constant quantity. The concentration of the chloride ions is given by that of the KCl and can be changed. Introducing $a_{Hg_2^{2+}} = K_{ap}/a^2_{Cl^-}$ in the previous equation, we get

$$\varphi_{Hg} = \overset{\circ}{\varphi}_{Hg} + \frac{RT}{2F} \ln K_{ap} - \frac{RT}{2F} \ln a^2_{Cl^-} = \varphi'^{\circ} - \frac{RT}{F} \ln a_{Cl^-} \quad (20.24)$$

The potential of a calomel electrode thus depends on the activity of the chloride ion, since the electrode is reversible with respect to the chloride ions.

At a given concentration of the chloride ions (i.e. the concentration of KCl) a calomel electrode has an absolutely definite potential and can serve as a reference electrode. Calomel electrodes are used with KCl concentrations equal to 1 *N* (a normal calomel electrode) and 0.1 *N* (a decinormal calomel electrode), and also with a saturated solution of KCl (a saturated calomel electrode). Their electrode potentials relative to a hydrogen electrode at a temperature close to a room temperature are expressed by the following equations (where *T* is the temperature, K):

$$\left.\begin{array}{ll} KCl;\ Hg_2Cl_2(s)\,|\,Hg; & \varphi = 0.3338 - 0.000\,07\,(T - 298) \\ c = 0.1 & \text{at } 0\,^\circ C\ \varphi = 0.3355;\ \text{at } 18\,^\circ C\ \varphi = 0.3343\ V \end{array}\right\} \quad (20.25)$$

$$\left.\begin{array}{ll} KCl;\ Hg_2Cl_2(s)\,|\,Hg; & \varphi = 0.2800 - 0.000\,24\,(T - 298) \\ c = 1 & \text{at } 0\,^\circ C\ \varphi = 0.2860;\ \text{at } 18\,^\circ C\ \varphi = 0.2817\ V \end{array}\right\} \quad (20.25a)$$

$$\left.\begin{array}{ll} KCl(sat.);\ Hg_2Cl_2(s)\,|\,Hg; & \varphi = 0.2415 - 0.000\,76\,(T - 298) \\ & \text{at } 0\,^\circ C\ \varphi = 0.2605;\ \text{at } 18\,^\circ C\ \varphi = 0.2468\ V \end{array}\right\} \quad (20.25b)$$

Silver-silver chloride electrodes can also be used as reference electrodes. An example of these electrodes is

$$HCl,aq;\ AgCl(s)\,|\,Ag$$

**20.7. Electrodes of the First and Second Kinds.** The process of migration of a cation from the metal into the solution or vice versa proceeds on metal electrodes immersed in a solution of a salt of this metal. The direction of migration depends on the sign of the e.m.f.

of the cell into which the electrode is included. Such electrodes are reversible relative to the cation. They are called *electrodes of the first kind*. The hydrogen electrode belongs to this kind. The potential of an electrode of the first kind is related to the activity of the cation in the solution by the Nernst equation (20.14).

*Electrodes of the second kind* are electrodes in which the metal is covered with a layer of poorly soluble salt of this metal and is in a solution saturated with this salt and containing another easily soluble salt with the same anion. Among these electrodes are the calomel electrode considered above and the widely used silver-silver chloride electrode, for each of which

$$\varphi = \varphi^\circ - \frac{RT}{F} \ln a_{Cl^-} \qquad (20.14a)$$

Electrodes of this kind are reversible with respect to the cation (for example, $Ag^+$) and to the anion ($Cl^-$), but only the concentration of the $Cl^-$ can be controlled, and only in this way is it possible to influence the concentration of the $Ag^+$ and, therefore, the electrode potential, using the Nernst equation.

The electrodes $Cl^- \mid Pt, Cl_2$, $Br^- \mid Pt, Br_2$ and others are reversible relative to the anion, but here the metal of the electrode exchanges only electrons with the electrolyte. It is more proper to consider such electrodes as oxidation-reduction ones (see Sec. 20.9).

**20.8. Standard Electrode Potentials in Aqueous Solutions.** Table 20.1 gives the standard potentials $\varphi^\circ$ of selected electrodes in aqueous

TABLE 20.1

**Standard Electrode Potentials in Aqueous Solutions (in V)**

| Electrode | $\varphi^\circ$, V | Electrode | $\varphi^\circ$, V |
|---|---|---|---|
| $Li^+ \mid Li$ | −3.045 | $Cu^{2+} \mid Cu$ | +0.337 |
| $K^+ \mid K$ | −2.925 | $Cu^+ \mid Cu$ | +0.521 |
| $Na^+ \mid Na$ | −2.714 | $I^- \mid I_2$ | +0.536 |
| $Mg^{2+} \mid Mg$ | −2.37 | $Pb^{4+} \mid Pb$ | +0.7 |
| $Al^{3+} \mid Al$ | −1.66 | $Hg_2^{2+} \mid Hg$ | +0.789 |
| $Zn^{2+} \mid Zn$ | −0.763 | $Ag^+ \mid Ag$ | +0.799 |
| $Fe^{2+} \mid Fe$ | −0.440 | $Hg^{2+} \mid Hg$ | +0.854 |
| $Cd^{2+} \mid Cd$ | −0.403 | $Br^- \mid Br_2$ | +1.065 |
| $Ni^{2+} \mid Ni$ | −0.250 | $OH^- \mid O_2$ | +0.401 |
| $Pb^{2+} \mid Pb$ | −0.126 | $Au^{3+} \mid Au$ | +1.29 |
| $H_3O^+ \mid H_2$ | 0.000 | $Cl^- \mid Cl_2$ | +1.360 |
| | | $F^- \mid F_2$ | +2.65 |

solutions. Since they are measured relative to the standard hydrogen electrode, the sign of the quantity $\varphi^\circ$ indicates the sign of the charge of this electrode and the sign of the e.m.f. of the entire cell which the electrode acquires when included in a cell with a hydrogen electrode

$$\mathrm{Pt,\ H_2 \mid \underset{a=1}{H^+} \parallel \underset{a=1}{Me^{2+}} \mid Me;} \qquad \varphi_{Me} = \varphi^\circ_{Me}$$

If $\varphi^\circ$ is negative for the electrode on the right, the current will flow from the left to the right in the outer circuit of the cell being considered, and from the right to the left inside the cell, which corresponds to the reaction

$$Me + H^+ \longrightarrow Me^+ + \frac{1}{2} H_2$$

The metal Me has a negative charge relative to the hydrogen electrode. If we connect an electrode having a positive value of $\varphi^\circ$ to a hydrogen electrode, the current inside the cell will flow from the left to the right in accordance with the reaction

$$Me^+ + \frac{1}{2} H_2 \longrightarrow Me + H^+$$

The table of standard potentials of metals is thus a quantitative expression of the displacement series of metals. Every metal displaces from solutions metals arranged below it in the table. The reverse sequence of displacement holds for non-metals. It should be remembered that the tabulated values relate to solutions with $a_+ = 1$. The table is a displacement series only for such solutions. If we take solutions with other concentrations, then metals with close values of $\varphi^\circ$ may change their relative position in the displacement series. Equations of type (20.15) and (20.24) make it possible to foresee such an event quantitatively.

Let us calculate the e.m.f. of a cell consisting of two electrodes $Me_1$ and $Me_2$ in solutions of the corresponding ions with the activities $a_1$ and $a_2$. The e.m.f. can obviously be calculated according to the following formula (the electrode $Me_2$ is on the left, $t = 25$ °C):

$$E = \varphi_2 - \varphi_1 = \varphi_2^\circ - \varphi_1^\circ + \frac{RT}{z_2 F} \ln a_{+,2} - \frac{RT}{z_1 F} \ln a_{+,1} =$$

$$= \varphi_2^\circ - \varphi_1^\circ + 0.0591 \log \frac{(a_{+,2})^{1/z_2}}{(a_{+,1})^{1/z_1}} \qquad (20.26)$$

Let us form the cell of the electrodes Fe | $Fe^{2+}$, aq and $Cd^{2+}$, aq | Cd:

$$\mathrm{Fe \mid Fe^{2+},\ aq \parallel Cd^{2+},\ aq \mid Cd}$$

The e.m.f. of this cell can be found from the equation

$$E = (-0.403 + 0.440) + \frac{0.0591}{2} \log \frac{a_{Cd^{2+}}}{a_{Fe^{2+}}}$$

For solutions with $a_{Cd^{2+}} = a_{Fe^{2+}}$ we have $E = +0.037$ V and the current in the cell (outer circuit) flows from the right to the left, i.e. the iron displaces the cadmium from the solution.

Let us find the conditions at which $E = 0$. This will obviously occur if

$$\log \frac{a_{Cd^{2+}}}{a_{Fe^{2+}}} = -\frac{0.037 \times 2}{0.0591} = -1.252; \quad \frac{a_{Fe^{2+}}}{a_{Cd^{2+}}} = 17.7$$

Assuming that $\frac{a_{Fe^{2+}}}{a_{Cd^{2+}}} = \frac{m_{Fe^{2+}}}{m_{Cd^{2+}}}$, we find that at a concentration of the cadmium ions of approximately one-eighteenth that of the iron ions the iron does not displace the cadmium from the solution. If the ratio $m_{Cd^{2+}}/m_{Fe^{2+}}$ is less than 1/18, the cadmium displaces the iron.

A comparison of elements far from each other in the table of standard potentials shows that reversal of the reaction of displacement is frequently practically impossible. Thus, for the pair Cu ($\varphi_2$) and $H_2$ ($\varphi_1^\circ = 0$) we have

$$E = \varphi_2 - \varphi_1 = \varphi_2^\circ + 0.0591 \log \frac{a_{Cu^{2+}}^{1/2}}{a_{H^+}} \tag{20.27}$$

At $E = 0$

$$\log \frac{a_{Cu^{2+}}^{1/2}}{a_{H^+}} = -\frac{0.345}{0.0591} = -5.837; \quad \frac{a_{Cu^{2+}}^{1/2}}{a_{H^+}} = 1.45 \times 10^{-6}$$

We once more take the ratio of the activities equal to that of the molalities. When $a_{H^+} = 10$ (in strong acids)

$$a_{Cu^{2+}} = (1.45 \times 10^{-5})^2 = 2 \times 10^{-10}$$

Thus at extremely low and uncontrollable concentrations of the copper ions $m_{Cu^{2+}} < 2 \times 10^{-10}$ the metal copper should displace $H^+$ from the solution, but the reaction will stop when this limiting concentration is reached[1].

A displacement reaction that can be carried out in an electrochemical cell proceeds spontaneously and irreversibly upon the direct contact of the more active metal with the solution of the less active one, since for such a reaction $\Delta G < 0$ when $E > 0$.

**20.9. Oxidation-Reduction Electrodes and Their Potentials.** Let us consider such electrodes on which the reactions are not connected with the liberation from the electrolyte or the dissolving in it of elements (metals, gases). The reception or giving up of electrons by the electrodes which is essential for electrochemical reactions naturally also occur in such cells, but these processes are connected with a change in the valence of the ions in the solution.

[1] Very low, but stable concentrations of free metal ions can be obtained by binding these ions into strong complex ions upon the introduction into the solution of a great excess of ions or molecules of a complex-forming agent.

When a platinum electrode is immersed into a solution containing iron ions with two and three charges, electrons leave the metal and join the iron ions with three charges:

$$Fe^{3+} + e \rightleftarrows Fe^{2+}$$

Metal platinum is convenient because its atoms do not participate in the electrode process, and it serves only as a carrier of electrons.

The electrode receives a positive charge and attracts anions from the solution. As a result an electrical double layer with a definite potential jump is formed on the surface of the electrode. This electrode potential depends on the concentration of the ions $Fe^{2+}$ and $Fe^{3+}$. The sign of the potential and its magnitude are determined relative to the standard hydrogen electrode potential:

$$(-)Pt,\ H_2 \mid HCl \mid\mid Fe^{2+},\quad Fe^{3+} \mid Pt(+)$$

$$p_{H_2} = 1\ a_{\pm} = 1$$

The following reaction proceeds in this cell:

$$\frac{1}{2} H_2 + Fe^{3+} = H^+ + Fe^{2+}$$

Let us write this reaction in a somewhat different way:

$$\frac{1}{2} H_2 + Fe^{3+} + 3Cl^- = \underbrace{H^+ + Cl^-} + \underbrace{Fe^{2+} + 2Cl^-}$$

The e.m.f. of the cell, equal to the electrode potential of the right electrode, is found by the equation

$$E = E^\circ - \frac{RT}{F} \ln \frac{a_{HCl} a_{Fe^{2+}}}{p_{H_2}^{1/2} a_{Fe^{3+}}} = E^\circ - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \qquad (20.28)$$

(according to the initial condition $p_{H_2} = 1$ and $a_{HCl} = 1$). $E^\circ = \varphi^\circ$ is the standard potential of the electrode $Fe^{2+}$, $Fe^{3+}$ | Pt at activities of the ions $Fe^{2+}$ and $Fe^{3+}$ equal to unity. At 25 °C we have $\varphi^\circ = +0.771$ V.

Let us replace the hydrogen electrode in the cell considered above with another electrode having a higher positive electrode potential than the electrode $Fe^{2+}$, aq; $Fe^{3+}$, aq | Fe. We can thus form a chemical cell on whose electrode $Fe^{2+}$, $Fe^{3+}$ a reaction of oxidation occurs, i.e.

$$Fe^{2+} \rightleftarrows Fe^{3+} + e$$

and electrons are given up to the electrode. On the second electrode a reaction takes place during which the charge of the cation decreases, i.e. a reduction reaction occurs. The current in the cell flows from the right to the left and the electrode $Fe^{2+}$, $Fe^{3+}$ has a negative charge (the e.m.f. of the cell is less than zero).

Connecting the electrode $Fe^{3+}$, $Fe^{2+}$ | Pt to another electrode having a lower positive potential than the electrode $Fe^{2+}$, $Fe^{3+}$, we obtain a cell in which a reaction of reduction will proceed on the electrode $Fe^{2+}$, $Fe^{3+}$ and electrons will migrate from the electrode into the solution. On the other electrode a reaction proceeds with the giving up of electrons to the electrode and an increase in the charge of the cations, i.e. a reaction of oxidation proceeds (the e.m.f. of the cell is greater than zero). The electrodes $Sn^{4+}$, $Sn^{2+}$ | Pt; $MnO_4^{2-}$ | $MnO_4^-$ | Pt and others behave similarly.

Thus the electrode considered above always participates in a summary oxidation-reduction reaction, the two halves of which (electrochemical reactions) proceed on two electrodes, one being an oxidation and the other a reduction reaction.

It can be understood from the foregoing why electrodes of the type $Fe^{3+}$, $Fe^{2+}$ | Pt and cells with such electrodes have been called oxidation-reduction ones. It must be underlined, however, that any electrochemical reaction includes the liberation or attachment of electrons and is an oxidation-reduction one. The ions always change their charge on the electrodes. Thus, on the electrodes of the Daniell-Jacobi cell

$$(-)\,Zn \mid ZnSO_4,\ aq \parallel CuSO_4,\ aq \mid Cu(+)$$

(see Table 20.1) the reduction reaction $Cu^{2+} + 2e \rightarrow Cu$ proceeds from the left to the right, and the oxidation reaction $Zn \rightarrow Zn^{2+} + 2e$ from the right to the left. The only feature characteristic of the cells and electrodes considered in the present section is the fact that the cations and anions, when changing their charge, are not liberated on the electrodes and do not appear in the solution as a result of migration from the electrode into the solution.

The term *oxidation-reduction* (cell, electrode, potential) can obviously be related to any case, and not only to the given one. A special term should have been introduced, but owing to its absence at present we retain the historically established term *oxidation-reduction* (cell, electrode, potential), although it is applied in a too narrow sense

The term *redox potential*, which is identical to the term *oxidation-reduction*, is frequently used to denote potentials of the type indicated above in literature on the subject.

Table 20.2 gives the values of selected standard oxidation-reduction potentials. The rule of signs for them ensues from the general postulates considered previously. Let us connect an oxidation-reduction electrode to a standard hydrogen one, placing the latter on the left. The e.m.f. of the cell formed in this way is considered to be positive and, therefore, the potential of the right electrode is positive if the current in the cell

$$Pt,\ H_2 \mid HA \parallel Me^{n+},\ Me^{m+},\ aq \mid Pt$$

TABLE 20.2

**Standard Oxidation-Reduction Potentials in Aqueous Solutions (in V)**

| Electrode | Electrode process | φ, V |
|---|---|---|
| $Cr^{2+}$, $Cr^{3+}$ \| Pt | $Cr^{3+} + e \rightleftarrows Cr^{2+}$ | −0.41 |
| $Sn^{2+}$, $Sn^{4+}$ \| Pt | $Sn^{4+} + 2e \rightleftarrows Sn^{2+}$ | +0.15 |
| $(ClO_3^- + 2OH^-)ClO_4^-$ \| Pt | $ClO_4^- + H_2O + 2e \rightleftarrows ClO_3^- + 2OH^-$ | +0.36 |
| $MnO_4^-$, $MnO_4^{2-}$ \| Pt | $MnO_4^- + e \rightleftarrows MnO_4^{2-}$ | +0.564 |
| $Fe^{2+}$, $Fe^{3+}$ \| Pt | $Fe^{3+} + e \rightleftarrows Fe^{2+}$ | +0.771 |
| $Hg_2^{2+}$, $2Hg^{2+}$ \| Pt | $2Hg^{2+} + 2e \rightleftarrows Hg_2^{2+}$ | +0.920 |
| $Mn^{2+}$, $Mn^{4+}$, $(+4OH^-)$ \| Pt | $MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{2+} + 2H_2O$ | +1.23 |
| $Pb^{2+}$, $Pb^{4+}$, $(+4OH^-)$ \| Pt | $PbO_2 + 4H^+ + 2e \rightleftarrows Pb^{2+} + 2H_2O$ | +1.455 |
| $Mn^{2+}$, $Mn^{3+}$ \| Pt | $Mn^{3+} + e \rightarrow Mn^{2+}$ | +1.51 |
| $PbO_2$, $PbSO_4$ \| Pt | $PbO_2 + SO_4^{2-} + 4H^+ + 2e \rightleftarrows PbSO_4 + 2H_2O$ | +1.685 |
| $Pb^{4+}$, $Pb^{2+}$ \| Pt | $Pb^{4+} + 2e \rightarrow Pb^{2+}$ | ~+1.7 |
| $Co^{2+}$, $Co^{3+}$ \| Pt | $Co^{3+} + e \rightarrow Co^{2+}$ | +1.82 |

flows from the left to the right, i.e. the reaction on the right electrode proceeds with the consumption of electrons and the ions decrease their positive charge, i.e. are reduced.

Oxidation-reduction potentials are measured with the aid of an indifferent platinum electrode. Since in a standard hydrogen electrode the current is also supplied by platinum, electrode potentials of this type do not include the Galvani potentials $Me_1 \mid Me_2$. If in measuring the oxidation-reduction potential an electrode made of another indifferent metal, for example gold, is used, the electrode potential includes the Galvani potential ${}_{Pt}\varphi_{Au}$ of the contact Pt|Au. The total electrode oxidation-reduction potential being measured relative to the standard hydrogen electrode remains unchanged, since it corresponds to the same process of migration of an electron from one ion to another. When platinum is replaced with gold, the jump on the electrode-solution interface will so change that the additional Galvani potential Pt | Au will be compensated.

**20.10. Quinhydrone Electrode.** Oxidation-reduction electrodes can also be formed on the basis of organic oxidation-reduction systems. Many such systems exist, but the *quinhydrone electrode* is of special interest. This is the name given to a platinum (or gold) electrode immersed in a solution of quinhydrone [a molecular compound of quinone and hydroquinone having the formula $C_6H_4O_2 \cdot C_6H_4(OH)_2$, which in a solution partly dissociates into quinone and hydroquinone].

Connecting a standard hydrogen electrode on the left of a quinhydrone electrode, we obtain a cell in which the following reaction proceeds:

$$C_6H_4O_2 + H_2 = C_6H_4(OH)_2$$

and on the right electrode the reaction

$$C_6H_4O_2 + 2H_3O^+ + 2e = C_6H_4(OH)_2 + 2H_2O$$

For the last reaction we obviously get [see Sec. 19.6, Eq. (19.3)][1]

$$\Delta G^\circ = -RT \ln K_p + RT \ln \frac{a_h}{a_q a_{H^+}^2}$$

$$E = \varphi_q = -\frac{\Delta G^\circ}{zF} = \frac{RT}{2F} \ln K_p - RT \ln \frac{a_h}{a_q a_{H^+}^2} =$$

$$= \varphi_q'^{\circ} + \frac{RT}{2F} \ln \frac{m_q a_{H^+}^2}{m_h} \qquad (20.29)$$

where $E$ = e.m.f. of a cell consisting of a standard hydrogen and a quinhydrone electrodes, equal to $\varphi_q$ (the potential of the quinhydrone electrode)

$m_q$ and $m_h$ = molalities of the quinone and hydroquinone in the solution, respectively.

Since the concentrations of these compounds are not great, the activities can be considered equal to the molalities. Usually the solution is saturated with quinhydrone and one of the compounds forming it—hydroquinone or quinone. In this case (according to the law of mass action) the concentrations of the hydroquinone and quinone in the solution at a given temperature are constant. Combining terms with logarithms of the constant quantities $m_q$ and $m_h$ into a common constant factor, we get an expression for $\varphi_{q,h}$ for such an electrode ($z = 2$)

$$\varphi_{q,h} = \left(\varphi_q'^{\circ} + \frac{RT}{2F} \ln \frac{m_q}{m_h}\right) + \frac{RT}{F} \ln a_{H^+} = \varphi_{q,h}^\circ + \frac{RT}{F} \ln a_{H^+} \qquad (20.30)$$

At 25 °C in a solution saturated with quinhydrone and hydroquinone the value of $\varphi_{q,h}^\circ = 0.6992$ V. Its dependence on the temperature is determined by the equation

$$\varphi_{q,h}^\circ = 0.7177 - 7.4 \times 10^{-4} t \qquad (20.31)$$

The quinhydrone electrode is easy to prepare and is convenient in operation. If we add some quinhydrone to a solution and immerse a platinum wire into it, a constant and reproduceable potential rapidly sets in. Measurement of this potential makes it possible to determine the activity of the hydrogen ions (hydroxonium) in the solution.

A quinhydrone electrode cannot be used in alkaline solutions. This is explained by the fact that hydroquinone is a weak acid.

[1] The concentration of the electrons in a definite metal electrode may be considered constant and the corresponding term in Eq. (20.29) is included in the term $\varphi_q^\circ$.

It greatly dissociates in an alkaline medium and its concentration in a saturated solution is not constant. This electrode also cannot be used in the presence of strong oxidizers or reducers.

A quinhydrone electrode is sometimes considered as a hydrogen one in which the concentration of hydrogen is determined by the equilibrium

$$\underset{\text{quinhydrone}}{C_6H_4O_2 \cdot C_6H_4(OH)_2} \rightleftarrows \underset{\text{quinone}}{2C_6H_4O_2} + H_2$$

The hydrogen obtained according to this reaction is adsorbed on the electrode and forms a hydrogen electrode. Use of Eq. (20.23) allows us to compute the pressure of gaseous hydrogen in equilibrium with such a hydrogen electrode

$$\varphi = \frac{RT}{F} \ln \frac{a_{H^+}}{p_{H_2}^{1/2}}$$

At $a_{H^+} = 1$ and 25 °C the standard potential of a quinhydrone electrode is equal to 0.699 V. Consequently

$$0.699 = -\frac{0.0591}{2} \log p_{H_2} \quad \text{and} \quad p_{H_2} = 10^{-24} \text{ atm}$$

The value $10^{-24}$ atm does not correspond to a pressure of the hydrogen having any real significance, and consideration of the quinhydrone electrode as a hydrogen one is purely formal.

**20.11*. Gas Electrodes. Thermodynamic Calculation of Potential of Oxygen Electrode.** We have already considered the hydrogen electrode and cells with this electrode. We can form a reversible chlorine electrode on platinum and set up the gas cell

$$(-)Pt,\ H_2 \mid HCl,\ aq \mid Cl_2,\ Pt(+)$$

where the following chemical reaction is the current forming process:

$$\frac{1}{2} H_2 + \frac{1}{2} Cl_2 = H^+ + Cl^-$$

Measuring the e.m.f. of this cell, we can compute $\Delta G$ for the formation of solutions of HCl from the gaseous elements.

The following electrochemical reaction should proceed on a reversible oxygen electrode:

$$O_2(g) \rightleftarrows O_2 \text{ (adsorbed on Pt)} \overset{+2H_2O}{\rightleftarrows} 4OH^- - 4e$$

The measured potential of the oxygen electrode differs from the one that should be expected on the basis of thermodynamic data ($E^\circ = 0.40$ V), since attempts to prepare a reversible oxygen electrode have not been successful[1].

After the preparation of an oxygen electrode the potential first grows rapidly, and then slowly, during several days. The final value of the potential is less than that calculated by the thermodynamic method (see below).

The value of $\varphi^\circ$ for the electrode Pt, $O_2 \mid OH^-$ given in tables is calculated indirectly. Using the equilibrium constants of the reaction

$$H_2 + \frac{1}{2} O_2 = H_2O(g) \qquad \text{(I)}$$

[1] Recently investigators succeeded in preparing a reversible oxygen electrode for the reaction $O_2 \rightarrow H_2O_2$ in an alkaline solution.

measured at elevated temperatures, after passing over from these temperatures to the standard one 25 °C we get

$$\Delta G_{\mathrm{I}}^{\circ} = -54\ 600 \text{ cal}$$

This value corresponds to statistically computed values of the entropies of the participants of reaction (I).

To calculate $\Delta G$ for the reaction of formation of liquid water

$$H_2O\ (g) \rightleftharpoons H_2O\ (lq) \qquad \text{(II)}$$

we use the values of the saturated vapour pressure of water $p_{25\ °C} = 23.7$ mm

$$\Delta G_{\mathrm{II}}^{\circ} = +4.575T \log p = +4.575 \times 298 \times \log \frac{23.7}{760} = -2050 \text{ cal}$$

Combining equilibria (I) and (II) (see Vol. 1, Sec. 8.11) by summation of Eqs. (I) and (II), we get

$$H_2 + \frac{1}{2} O_2 = H_2O(lq) \qquad \text{(III)}$$

$$\Delta G_{\mathrm{III}}^{\circ} = \Delta G_{\mathrm{I}}^{\circ} + \Delta G_{\mathrm{II}}^{\circ} = -56\ 650 \text{ cal}$$

We can find the value of $\Delta G_{\mathrm{III}}^{\circ}$ in a different way, for example by combining the data for the equilibria

$$Hg + \frac{1}{2} O_2 = HgO(s) \text{ (pressure of dissociation of HgO)}$$

$$H_2 + HgO = H_2O(lq) + Hg \text{ (e.m.f. of the corresponding cell)}$$

The mean value obtained from different data for expression (III) is $\Delta G_{\mathrm{III}}^{\circ} = -56\ 700$ cal.

Hence for the gas cell

$$\underset{1\ \text{atm}}{(-)Pt,\ H_2} \mid \underset{a=1}{HCl + aq} \mid \underset{1\ \text{atm}}{O_2,\ Pt(+)}$$

$$E = \varphi(O_2, H^+) = -\frac{\Delta G_{\mathrm{III}}^{\circ}}{2F} = +\frac{56\ 700}{2 \times 23\ 062} = 1.229 \text{ V}$$

In a solution of HCl, however, the activity of the ions $OH^-$ is determined from a constant value (at 25 °C) of $a_H a_{OH} = 1.008 \times 10^{-14}$ in solutions of an average concentration. Hence for the standard oxygen electrode

$$\begin{array}{l|l} OH^- & O_2,\ Pt \\ a_{OH^-} = 1 & 1\ \text{atm} \end{array}$$

we have

$$\varphi_{O_2,\ Pt}^{\circ} = \varphi_{O_2,\ Pt} + RT \ln a_{OH^-} = 1.229 + 0.059\ 15 \times \log 1.008 \times 10^{-14}$$

whence

$$\varphi_{O_2,\ Pt}^{\circ} = 0.401 \text{ V}$$

**20.12*. Standard Electrode Potentials in Non-Aqueous Solutions.** For non-aqueous electrolytes the values of the standard potentials $\varphi^{\circ}$ differ from the corresponding ones for aqueous solutions. Great difficulties appear in comparing the values of $\varphi^{\circ}$ for determining the electrochemical reactions in various solvents. These are connected with the potentials at the interfaces between two liquids.

For this reason the accurately measured values of $\varphi^\circ$ are the ones measured in a solvent and related to the standard hydrogen electrode in the same solvent whose potential is equated to zero. The values of $\varphi^\circ$ are calculated in the same way as for aqueous solutions (see Sec. 20.6).

TABLE 20.3

**Standard Electrode Potentials $\varphi^\circ$ in Non-Aqueous Solvents Related to the Standard Hydrogen Electrode in the Same Solvent (in V)**

| Electrode | Standard electrode potentials, $\varphi^\circ$ (25 °C) | | | | | |
|---|---|---|---|---|---|---|
| | in $H_2O$ | in HCOOH | in $CH_3OH$ | in $C_2H_5OH$ | in $NH_3$ (lq) at −50 °C | in $CH_3CN$ |
| $Li^+ \mid Li$ | −2.96 | −3.48 | −3.095 | −3.04 | −2.24 | −3.23 |
| $K^+ \mid K$ | −2.92 | −3.36 | −2.920 | −2.847 | −1.98 | −3.16 |
| $Na^+ \mid Na$ | −2.71 | −3.42 | −2.778 | −2.675 | −1.85 | −2.87 |
| $Rb^+ \mid Rb$ | −2.93 | −3.45 | — | — | −1.93 | −3.17 |
| $Ca^{2+} \mid Ca$ | −2.77 | −3.20 | — | — | −1.64 | −2.75 |
| $Zn^{2+} \mid Zn$ | −0.76 | −1.05 | −0.74 | −0.64 | −0.53 | −0.74 |
| $H^+ \mid H_2$ | ±0.00 | ±0.00 | ±0.00 | ±0.00 | ±0.00 | ±0.00 |
| $Cu^{2+} \mid Cu$ | +0.52 | −0.14 | +0.490 | +0.21 | — | −0.28 |
| $I^- \mid I_2$ | +0.54 | — | +0.357 | +0.305 | +1.43 | +0.07 |
| $Hg^{2+} \mid Hg$ | +0.79 | +0.18 | +0.74 | +0.76 | +0.75 | — |
| $Ag^{2+} \mid Ag$ | +0.80 | +0.17 | +0.764 | +0.749 | +0.83 | +0.58 |
| $Br^- \mid Br_2$ | +1.07 | — | +0.837 | +0.777 | +1.83 | +0.47 |
| $Cl^- \mid Cl_2$ | +1.34 | +0.99 | +1.116 | +1.048 | +2.03 | +0.58 |

Table 20.3 gives the standard potentials of selected electrodes in pure methyl and ethyl alcohols at 25 °C and in liquid ammonia at −50 °C with respect to a standard electrode in the same solvents. The values of $\varphi^\circ$ for aqueous solutions are given for purposes of comparison. The differences between the potentials in water and in alcohols are not great. The values of the potentials differ for ammonia, but the sequence of arrangement of the electrodes is mainly the same, with a few exceptions.

Calculation of the standard potentia l of an electrode in a non-aqueous solution with respect to the standard hydrogen electrode in an aqueous solution is quite complicated. As indicated above, this involves great difficulties and is performed in various ways on the basis of different assumptions[1].

[1] For example, V. Pleskov proposed to consider the potential of a rubidium electrode the same in all solvents. N. Izmailov proposes to compute the change in the Gibbs energy (the work done in the transition of an ion from an infinitely dilute non-aqueous solution to an infinitely dilute aqueous one and hence the corresponding potential jump) according to the energies of solvation of the ion in the two solutions. He calculates the latter quantity from experimental data for the sum of the two ions on the basis of extrapolation of the values to an infinitely low reciprocal value of the sum of the radii of the ions in a series of salts of the same type with a common ion (see Sec. 22.10).

# CHAPTER 21

# ELECTROCHEMICAL CELLS

**21.1. Classification of Cells.** All electrochemical cells are distinguished according to two features:

1. The summary process underlying the functioning of the cell. This process may be a chemical one or a process of levelling out of the concentrations of two electrolytes which are solutions of the same substance. According to this feature all electrochemical cells are divided into *chemical* and *concentration* ones.

2. The presence or absence of diffusion or (more broadly) liquid junction potentials. When diffusion potentials are present we have a *cell with transport* or *transference*. When these potentials are absent we have a *cell without transference*.

The properties indicated in paragraphs 1 and 2 are not related. Depending on the combination of the properties listed above, we can obtain electrochemical cells of four kinds. It should be noted that the cells of all these kinds differ from one another not in the nature of the electrode processes, but in the nature of the summary process.

The thermodynamic laws for chemical and concentration cells without transference will be considered in the following section, and then we shall examine the difference between cells with and without transference, i.e. the part played by the diffusion potentials. Certain special kinds of cells described in later sections are also included in the classification given above. Their separate consideration is determined only by a peculiarity of the phase state or the valence transitions. These include gas cells in which the substances of the electrodes entering into electrode reactions are in the gaseous state and in which the pressure plays a significant role. The so-called oxidation-reduction cells (and electrodes) are chemical ones. The basic classification of electrochemical cells takes only two features into consideration, as was mentioned at the beginning of this section.

**21.2. Concentration Cells.** A *concentration cell* is one in which work of an electric current is obtained, when the external circuit is closed, in the process of transfer of a substance with the spontaneous levelling out of the concentration between two electrolytes—solutions of the same substance, or between two metal solutions—

electrodes, or in the levelling out of the pressures of two gas electrodes. There is no summary chemical process in a concentration cell. The design of the cell prevents the direct irreversible levelling out of the concentrations by diffusion and facilitates reversible levelling out, in which work ($-\Delta G$) of the electric current is produced.

A concentration cell consists of identical metal or gas electrodes immersed in electrolytes of different concentrations (activities) containing a salt of the same metal. An example is the cell ($a' > a''$)

$$\underset{p_1}{(-)\mathrm{Pt},\ \mathrm{H_2}}\ |\ \underset{a''}{\mathrm{HCl}}\ ||\ \underset{a'}{\mathrm{HCl}}\ |\ \underset{p_1}{\mathrm{H_2},\ \mathrm{Pt}(+)} \qquad \text{(a)}$$

In the functioning of this concentration cell, both electrodes do not undergo any thermodynamic change, since equal amounts of hydrogen pass into the solution at the left electrode and are liberated from the solution at the right one. Simultaneously the amount of HCl grows in the left electrolyte, and decreases in the right one. Thus the only result of the summary process is the transference of the solute (HCl) from the right solution to the left one, i.e. from the more concentrated to the more dilute one. This process is spontaneous and is therefore accompanied by a reduction in the Gibbs energy. It may proceed irreversibly without the performance of work by diffusion. In the cell, however, the process is reversible, and work of the electric current is produced.

The calculation of the maximum work of transference of a substance is made complicated by the potential jump at the interface between the two solutions, which is called the *liquid junction potential* or in a particular case the *diffusion potential*. To avoid the appearance of a diffusion potential, let us replace cell (a) with a more complicated one and put a new electrode immersed in its own solution between the two solutions of HCl:

$$\underset{\varphi_1}{(-)\mathrm{Pt},\ \mathrm{H_2}}\ |\ \underset{a''}{\mathrm{HCl}}\ ||\ \underset{a''}{\mathrm{HCl}},\ \underset{\varphi_2}{\mathrm{Hg_2Cl_2(s)}}\ |\ \underset{\varphi_3}{\mathrm{Hg}}\ |\ \underset{a''<a'}{\mathrm{Hg_2Cl_2(s)}},\ \underset{a'}{\mathrm{HCl}}\ ||\ \underset{a'}{\mathrm{HCl}}\ |\ \underset{\varphi_4}{\mathrm{H_2},\ \mathrm{Pt}(+)} \qquad \text{(b)}$$

This complex cell consists of two elementary cells whose e.m.f.s are opposed to each other and which differ only in the concentration of the HCl in each of them. At the boundaries || there are no diffusion potentials, since the contacting solutions are practically identical in composition.

Seeing that the electrode processes in the left and right cells are identical and directed oppositely, the only result of the operation of the complex cell is the transference of HCl from the right solution to the left one. Indeed, the following reactions take place in the cells (accompanied by the transfer of $F$ coulombs of electricity):

in the right cell

$$\mathrm{Hg} + \mathrm{H^+Cl^-}(a') = \frac{1}{2}\,\mathrm{Hg_2Cl_2(s)} + \frac{1}{2}\,\mathrm{H_2}$$

in the left one

$$\frac{1}{2}H_2+\frac{1}{2}Hg_2Cl_2(s)=Hg+H^+Cl^-(a'')$$

The summary process is

$$H^+Cl^-(a') \rightarrow H^+Cl^-(a'')$$

Let us calculate the change in the Gibbs energy $\Delta G$ when the solute is transferred from the solution of higher activity $a'$ to the solution of lower activity $a''$.

Two gramme-ions ($H^+$ and $Cl^-$) are transferred:

$$-EF=\Delta G=(\mu''_+-\mu'_+)+(\mu''_--\mu'_-)=$$

$$=RT\ln\frac{a''_+}{a'_+}+RT\ln\frac{a''_-}{a'_-}=RT\ln\frac{a''_+a''_-}{a'_+a'_-}=2RT\ln\frac{a''_\pm}{a'_\pm} \qquad (21.1)$$

whence

$$E=\frac{2RT}{F}\ln\frac{a'_\pm}{a''_\pm} \qquad (21.2)$$

In the more general case dissociation follows the scheme

$$C_{\nu_+}A_{\nu_-}=\nu_+C^{z_+}+\nu_-A$$

where $\nu_+z_+=\nu_-z_-$.

Reasoning as above, we get for the complex cell (b) an expression similar to Eq. (21.2):

$$E=\frac{z_++z_-}{z_+z_-}RT\ln\frac{a'_\pm}{a''_\pm}=yRT\ln\frac{a'_\pm}{a''_\pm} \qquad (21.2a)$$

where $y=(z_++z_-)/z_+z_-$.

Thus the work of an electric current in concentration cells is the work of a diffusion process that proceeds reversibly and consists of several (in our case four) reversible electrode processes differing in direction. Each electrode process is accompanied by a definite maximum work (decrease in $G$), and only the difference between these quantities is equal to the work of transference of the dissolved salt.

Besides the derivation of the e.m.f. of a cell without transference given above and based on a consideration of only the summary process of transference of the salt from $a''$ to $a'$, we can compute the e.m.f. of this cell as the sum of all four electrode potentials [denoted $\varphi_1$, $\varphi_2$, $\varphi_3$ and $\varphi_4$ in scheme (b)]. The potentials are taken with the signs that correspond to the arrangement of the electrode in the cell. The potentials $\varphi_2$ and $\varphi_3$ are considered as those of electrodes of the second kind reversible with respect to $Cl^-$

$$\varphi_1=-\varphi_1^\circ-\frac{RT}{F}\ln a''_+(H^+)$$

$$\varphi_2=+\varphi_2^\circ-\frac{RT}{F}\ln a''_-(Cl^-)$$

$$\varphi_3 = -\varphi_2^\circ + \frac{RT}{F} \ln a'_- (Cl^-)$$

$$\varphi_4 = +\varphi_1^\circ + \frac{RT}{F} \ln a'_+ (H^+)$$

$$E = \sum \varphi = \frac{RT}{F} \ln \frac{a'_+ a'_-}{a''_+ a''_-} = \frac{2RT}{F} \ln \frac{a'_\pm}{a''_\pm} \qquad (21.3)$$

A glance at Eq. (21.1) shows that the measurement of the e.m.f. of concentration cells is a very convenient method of determining the activity of a salt in solution ′ if it is known in solution ″.

An example of a different kind of concentration cell is one with two hydrogen electrodes under different pressures immersed into solutions with identical activities ($a''_\pm = a'_\pm$). Its e.m.f. is expressed by the equation

$$E = \varphi_2 - \varphi_1 = -\frac{RT}{F} \ln \left(\frac{p''}{p'}\right)^{1/2} = -\frac{RT}{2F} \ln \frac{p''}{p'} \qquad (21.4)$$

Measurements of the value of $E$ for a cell in which the pressure of the hydrogen at one of the electrodes was changed up to 1000 atm showed the good applicability of the above equation up to $p = 200$ atm. At higher pressures the calculated value of $E$ is lower than the experimental one. It is obviously necessary to replace $p$ in Eq. (21.4) by the thermodynamic fugacity $f$, which at high pressures is greater than the pressure for hydrogen.

Concentration cells with hydrogen electrodes of the kind considered above can be used to determine the partial pressure of hydrogen in mixtures with inert gases (nitrogen, argon, etc.), i.e. for analysing gas mixtures.

Concentration cells can also be prepared in which the electrodes are solutions (liquid or solid) of the same metal in another, more positive one (for example, mercury amalgams) having different concentrations. These electrodes are immersed into a single common electrolyte, which may be an aqueous solution or a melt (a mixture of molten salts).

**21.3. Diffusion Potentials.** The mechanism of appearance of a diffusion potential is connected with diffusion of the ions of a salt in a solution against the gradient of concentration.

Let us apply Fick's first law and the expression for the absolute mobility of ions as their velocities at unit field strength to the diffusion of electrolyte ions in the zone of the gradient of concentration. This permits us to neglect the internal friction of the ions and obtain an equation relating the diffusion coefficient of an ion $D_i$ to its absolute mobility $u_i$ or mobility $U_i$

$$D_i = \frac{RTu_i}{z_i F} = \frac{RTU_i}{z_i F^2} \qquad (21.5)$$

The diffusion coefficient of the solute $D$ can be expressed through the mobilities and diffusion coefficients of the ions into which this solute dissociates:

$$D = \frac{2UV}{z_+z_-F^2(U+V)} = \frac{2D_i^+D_i^-}{D_i^+ + D_i^-} \tag{21.6}$$

Ions having a higher mobility diffuse into the more dilute solution with a greater velocity, and the boundary between the two solutions is charged with the sign of these ions at the side of the more dilute solution and with the reverse sign at the side of the concentrated one. An electrical double diffuse layer is formed with the corresponding potential jump. The appearing potential difference will accelerate the motion of a slowly moving ion and retard the motion of a rapidly moving one until a stationary state sets in. The velocities of the diffusing ions become equal and the solute begins to diffuse as a single whole. Thus further mutual moving away of the charges stops. The potential difference that sets in in the boundary layer between two solutions is called the *diffusion* or *liquid junction potential*.

The value of the diffusion potential as a function of the concentration can be determined in the simplest case—for the contact of two solutions of the same salt having different concentrations. The thermodynamic method makes it possible to determine the e.m.f. of a concentration cell as a whole with account taken of the diffusion potential.

Let us consider the migration of ions in the concentration cell ($a'' < a'$)

$$(-)\,\mathrm{Ag}\,|\,\underset{a''}{\mathrm{AgNO_3}}\,||\,\underset{a'}{\mathrm{AgNO_3}}\,|\,\mathrm{Ag}\,(+)$$

When $F$ coulombs of electricity pass through the cell, the following changes occur in the left half-cell: (1) one gramme-equivalent of silver dissolves; (2) $t_+$ g-eq of $Ag^+$ migrate to the right; (3) $t_-$ g-eq of $NO_3^-$ migrate from the right. Altogether $1 - t_+ = t_-$ g-eq of $Ag^+$ and $t_-$ g-eq of $NO_3^-$ appear in the left half-cell. Similar reasoning shows that during this time $t_-$ g-eq of each of the two ions disappear in the right half-cell.

Thus the summary process consists in the transference of $t_-$ g-eq of the two ions from the solution having the activity $a'$ to that having the activity $a''$.

The change in the Gibbs energy of this process in accordance with the general expression (21.1) will be

$$\Delta G = t_-RT\ln\frac{a''_+}{a'_+} + t_-RT\ln\frac{a''_-}{a'_-} = t_-2RT\ln\frac{a''_\pm}{a'_\pm} = -FE \tag{21.7}$$

$$E = 2t_-\frac{RT}{F}\ln\frac{a'_\pm}{a''_\pm} = 2\frac{V}{U+V}\frac{RT}{F}\ln\frac{a'_\pm}{a''_\pm} \tag{21.8}$$

The same result is obtained for cell (a) (p. 529), where $t_-$ is the transport number of $Cl^-$ in a solution of HCl. If there were no diffusion potential, i.e. the velocities of ions of different signs were the same, we would have $t_- = 0.5$ and $2t_- = 1$, and

$$E_{\text{conc}} = \frac{RT}{F} \ln \frac{a'_\pm}{a''_\pm} \tag{21.8a}$$

In this case the e.m.f. of a concentration cell with transference [of kind (a)] would be equal to the value of $E$ from Eq. (21.2), but without the factor 2, since in the process described by Eq. (21.8a), the passage of $F$ coulombs of electricity results in the transference of 0.5 g-eq of ions of each species, altogether 1 g-eq.

Comparing once more Eqs. (21.2) and (21.8), we see that although in a cell without transference (b) the presence of a calomel electrode does not affect the nature of the summary chemical process, the value of the e.m.f. according to Eq. (21.2) is double the e.m.f. value of a cell without the calomel electrode, i.e. of a cell with transference (a) [Eq. (21.8a)], if in the particular case the diffusion potential were absent (at $t_- = 0.5$). The matter is that in a cell of kind (b) the ion $Cl^-$ is transferred from one solution to the other by the solution and precipitation of solid $Hg_2Cl_2$. The quantity of electricity $F$ passing from one electrode to the other is equivalent to the transference of only a gramme-ion of $H^+$ from one solution to the other. The actual work of transference of $H^+Cl^-$ is two times greater.

Let us represent the e.m.f. of a cell as the sum of the concentration e.m.f. proper $E_{\text{conc}}$ and the diffusion potential $E_d$:

$$E = E_{\text{conc}} + E_d$$

we get

$$E_d = E - E_{\text{conc}} = \left(2\frac{V}{U+V} - 1\right)\frac{RT}{F} \ln \frac{a'_\pm}{a''_\pm} \tag{21.9}$$

or

$$E_d = (2t_- - 1)\frac{RT}{F} \ln \frac{a'_\pm}{a''_\pm} \tag{21.10}$$

If $V > U$, i.e. the mobility of an anion is greater than that of a cation, $E_d > 0$, i.e. the diffusion potential is added to the difference of the electrode potentials. If $V < U$, then the diffusion potential has the reverse sign relative to $E_{\text{conc}}$ and is subtracted from the electrode potential. The value of $E_d$ is not great. For solutions whose concentration ratio is 10, the value of $E_d$ is within the limits of $\pm 30$ mV at $t_- = 0.20$-$0.70$. For KCl the transport number is close to 0.5, and at $m'_\pm : m''_\pm = 10 : 1$ the value of $E_d = 1$ mV.

We have found an expression for the diffusion potential at the boundary between two solutions of one salt having different concentrations. Another particular case is the boundary between two solutions of different salts with a common

ion having the same concentration. In this case the diffusion potential appears owing to the difference in the mobilities of different ions in the two solutions. It is expressed by the formula

$$E_d = \frac{RT}{F} \ln \frac{U_1 + V_1}{U_2 + V_2} \tag{21.11}$$

A more general equation for the diffusion potentials in mixed solutions was derived by E. Henderson. He assumed that in the diffuse layer the composition of a mixed solution is linearly related to the distance from the interface and obtained the equation

$$E_d = \frac{RT}{F} \frac{(U' - V') - (U'' - V'')}{(U_1' - V_1') - (U_1'' - V_1'')} \ln \frac{U_1' + V_1'}{U_1'' + V_1''} \tag{21.12}$$

where

$$U' = \sum m_i U_i';$$

$$V' = \sum m_i V_i';$$

$$U_1' = \sum z_i m_i U_i';$$

$$V_1' = \sum z_i m_i V_i'$$

and the corresponding notation is used for the solution".

In all the cases dealt with, the transport number $t_-$ was considered to be independent of the concentration. If account is taken of the dependence of the transport number on the concentration, differential equations for the diffusion potential can be obtained. Let us consider the simple case when two solutions of the same salt are in contact. Let us imagine a zone of variable concentration divided into thin parallel layers. Within the limits of each layer the concentration of the $i$-th ion changes by $dm_i$, and its activity by $da_i$. When one faraday of electricity flows through a thin layer, $t_+$ g-eq of cations are transferred in one direction, and $t_-$ g-eq of anions in the other one. The ions of each species change their chemical potential by $d\mu_i = RT\, d \ln a_i$. The change in the Gibbs energy $dG$ upon the transfer of ions of all the species through a thin layer of the zone of variable concentration will be

$$dG = \sum t_{+i}\, RTd \ln a_{+i} - \sum t_{-i} RTd \ln a_{-i}$$

The total change $\Delta G$ for the entire diffuse layer will be

$$\Delta G = -FE_d = RT \int_{m_1}^{m_2} \left( \sum_i t_{+i} d \ln a_{+i} - \sum_i t_{-i} d \ln a_{-i} \right) \tag{21.13}$$

For a binary electrolyte Eq. (21.13) is simplified:

$$E_d = \frac{RT}{F} \int_{m_1}^{m_2} t_+ d \ln a_+ - \frac{RT}{F} \int_{m_1}^{m_2} t_- d \ln a_- \tag{21.13a}$$

If two electrolytes with different solvents are in contact, the difference in the properties of these solvents results in the appearance of a diffusion potential whose magnitude does not obey the equations considered above.

Electrochemical cells with diffusion potentials, the magnitude of whose e.m.f. is affected by the transport numbers, are called

*cells with transference*. Accurate calculation of diffusion potentials is impossible in the general case or requires that the transport numbers be known as a function of the concentration. This makes it difficult to use concentration cells with transference [kind (a) (p. 529)] for calculating the activities of dissolved salts. For this reason it is very important to set up concentration cells without diffusion potentials, i.e. cells without transference [kind (b) (p. 529)].

In measurements of a low accuracy the diffusion potential on the boundary between two solutions can be appreciably reduced by including between them a so-called *salt bridge*. The latter is a concentrated electrolyte, for example a strong solution of KCl or $NH_4NO_3$. The sharp reduction in the diffusion potential in this case is due to the fact that the ions of the concentrated solution conduct practically the entire current in the zones of contact, and the transport numbers of these salts are close to 0.5.

In addition, the introduction of a salt bridge causes two potentials of a smaller magnitude to appear instead of one diffusion potential at the initial boundary. Also, these two potentials are frequently opposite in sign.

The same object is achieved by introducing an indifferent salt into all the solutions of the cell. For accurate measurements cells without transference must be used.

**21.4*. Liquid Junction Potentials.** If two electrolytes with different immiscible solvents are in contact, a potential jump is observed whose properties differ from those of the diffusion potential described in the previous section. The diffusion potential disappears after the diffusion of the ions through the surface of contact stops and the concentration of the ions levels out. When different immiscible solvents come into contact, however, a constant equilibrium liquid junction potential[1] sets in (after equilibrium distribution of the coexisting liquid solutions is achieved).

Thus, in the electrochemical cell

$$\underset{\varphi_1}{\mathrm{Pt,\ H_2}} \mid \mathrm{HCl}(m_1) \underset{\text{water}}{\parallel} \underset{\varepsilon}{\mathrm{HCl}(m_2)} \underset{\text{phenol}}{\mid} \underset{\varphi_2}{\mathrm{H_2,\ Pt}} \qquad \text{(I)}$$

a potential difference $\varepsilon$ appears at the water-phenol interface, and the e.m.f. of the cell as a whole should be equal to the sum of three potentials:

$$E = \varphi_1 - \varphi_2 + \varepsilon \qquad (21.14)$$

where $\varepsilon$ is the liquid junction potential (the potential difference between two immiscible solutions).

The potentials of hydrogen electrodes in solutions of HCl in water and phenol are expressed, respectively, by the following equations:

$$\varphi_1 = \varphi_1^\circ + \frac{RT}{F} \ln a_{H^+}(\mathrm{w}) \qquad (21.15)$$

$$\varphi_2 = \varphi_2^\circ + \frac{RT}{F} \ln a_{H^+}(\mathrm{ph}) \qquad (21.16)$$

[1] The potentials on the boundaries of contact of any two solutions can be called liquid junction ones. The diffusion potentials of two electrolytes in one solvent are a particular case of liquid junction potentials.

where $a_{H^+}$ (w) and $a_{H^+}$ (ph) are the activities of $H^+$ in solutions in water and phenol ($\varphi_1^\circ \neq \varphi_2^\circ$).

Since the potential jump $\varepsilon$ sets in after equilibrium is reached in the distribution between the two liquids, the total e.m.f. $E$ is equal to zero. This is due to the fact that the transference of a substance from one phase to another is not connected with a decrease in the Gibbs energy. Hence, on condition that $E = 0$, from Eqs. (21.14), (21.15) and (21.16) we get

$$\varepsilon = \varphi_2 - \varphi_1 = \varphi_2^\circ - \varphi_1^\circ + \frac{RT}{F} \ln \frac{a_{H^+}(\text{ph})}{a_{H^+}(\text{w})} = k + \frac{RT}{F} \ln \frac{a_{H^+}(\text{ph})}{a_{H^+}(\text{w})} \qquad (21.17)$$

The quantity $k$ is equal to the difference of the standard potentials between two electrodes that vary only in being immersed into solutions with different solvents, but have such concentrations that in each solution the activity $a$ would be equal to unity. It is impossible to measure the absolute value of the quantity $k$.

It is possible to prepare electrochemical cells whose total e.m.f. in the first approximation is determined by the difference between two liquid junction potentials. An example is the cell

$$\begin{array}{ccccccccccc} \text{I} & & \text{II} & & \text{III} & & \text{IV} & & \text{V} & & \\ \text{Hg} \mid \text{Hg}_2\text{Cl}_2(\text{s}), & \text{HCl}(m_1) & \parallel & \text{HCl}(m_2) & \parallel & \text{HCl}(m_3) & \parallel & \text{HCl}(m_4) & \parallel & \text{HCl}(m_1), & \\ & \text{water} & & \varepsilon' \text{ phenol} & & \text{phenol} & \varepsilon'' & \text{water} & & \text{water} & \\ & & & & & \text{VI} & & & & & \\ & & & & & \text{Hg}_2\text{Cl}_2(\text{s}) \mid \text{Hg} & & & & & & \end{array} \qquad (\text{II})$$

The potentials I and VI are equal in magnitude and have opposite signs. If we take into consideration that the diffusion potentials III and V are generally small, then the e.m.f. of the cell is mainly determined by the liquid junction potentials at boundaries II and IV ($\varepsilon'$ and $\varepsilon''$) with an accuracy equal to the values of the diffusion potentials III and V

$$E = \varepsilon' - \varepsilon'' = \frac{RT}{F} \ln \frac{a_{H^+}(2)}{a_{H^+}(1)} - \frac{RT}{F} \ln \frac{a_{H^+}(3)}{a_{H^+}(4)} \qquad (21.18)$$

Since the activity coefficients of separate ions are thermodynamically indeterminable, frequently the mean activity coefficients of the electrolyte as a whole are used instead of them. For example, it is conventionally assumed that

$$\gamma'_{H^+} = \gamma'_{\pm HCl}$$

Hence it follows that

$$a_{H^+} = \gamma'_{H^+} m_{H^+} = \gamma'_{\pm HC}\, m_{H^+} \qquad (21.19)$$

Introducing this equality into Eq. (21.18), we get for the e.m.f. of cell (II) as a whole

$$E = \varepsilon' - \varepsilon'' = \frac{RT}{F} \ln \frac{m_{H^+}(2)\, \gamma'_{\pm HCl}(2)}{m_{H^+}(1)\, \gamma'_{\pm HCl}(1)} - \frac{RT}{F} \ln \frac{m_{H^+}(3)\, \gamma'_{\pm HCl}(3)}{m_{H^+}(4)\, \gamma'_{\pm HCl}(4)} \qquad (21.20)$$

**21.5*. Membrane Equilibria.** A special kind of electrochemical equilibrium between two liquid phases (electrolytes) separated by a membrane may appear when a membrane is impermeable to some of the ions which the solutes dissociate into. Thus, many membranes are impermeable to large organic ions, for example to the ions of acids with a high molecular mass. Equilibria of this kind can be characterized by the difference of electrical potentials or by the difference of

hydrostatic pressures at both sides of the membrane. Such equilibria are called *membrane equilibria*. They are also frequently called *Donnan equilibria* after F. Donnan who was the first to investigate the thermodynamic laws of the corresponding phenomena.

Let us consider a very simple example of membrane equilibrium for aqueous solutions of $Me^+R^-$ (solution *a*) and $Me^+A^-$ (solution *b*) separated by a membrane. The latter is permeable to the solvent, the cation $Me^+$ and the anion $A^-$ and is impermeable to the anion $R^-$. The initial state is shown in diagram *I* (Fig. 21.1), in which $m_i$ is the molality of the ions. It is quite obvious that in this non-equilibrium system MeA should diffuse through the membrane from the right to the left until equilibrium is reached, which the migration of $x$ moles of MeA corresponds to. The concentrations (molalities) of the ions in equilibrium are shown in diagram *II*.

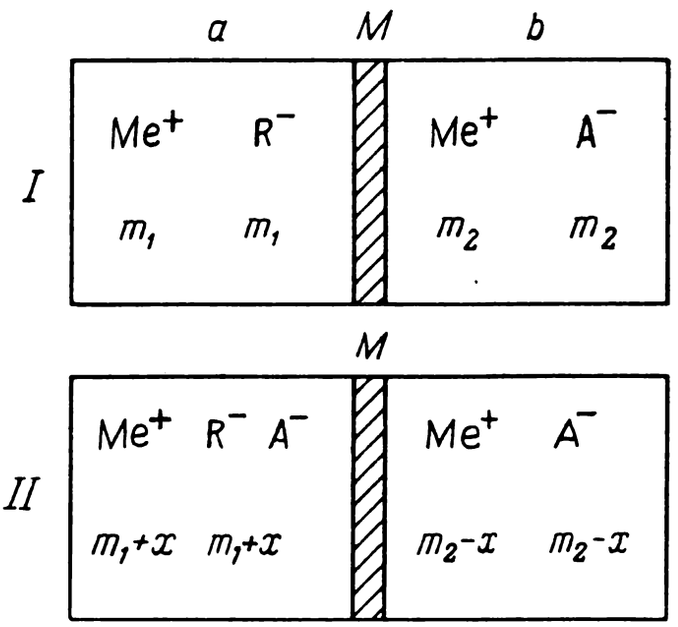



Fig. 21.1. Membrane equilibrium: *I*—initial state; *II*—equilibrium state

Let us consider the conditions of equilibrium between the two parts (*a*) and (*b*) of the system (see Fig. 21.1). Let the concentrations of $Me^+$, $A^-$ and $R^-$ at both sides of the membrane reach the values shown in diagram *II* when there is equilibrium between (*a*) and (*b*), and the pressures in the two parts of the system have the values $p^{(a)}$ and $p^{(b)}$. That is, we have an equilibrium pressure jump $p^{(a)}-p^{(b)}$ at membrane *M*. This pressure jump is called the *osmotic pressure* $\Pi$ of solution (*a*) with respect to solution (*b*). In addition, a membrane jump of the electrical potential may form.

Assume that the partial volumes of the solvent and the ions $Me^+$ and $A^-$ do not depend on the pressure and composition of the solution. Hence migration of the solvent or the ions $Me^+$ and $A^-$ through the membrane will not result in a total change in the volume of the system. In this case we can use the Helmholtz energy $A = f(V, T, x)$ for investigating the equilibrium state. The full differential of the Helm holtz energy should be equal to zero in equilibrium.

The transfer of one mole of a neutral solvent through the membrane with a jump in the electrical potential is not connected with a change in the Helmholtz energy. The pressure gradient should be taken into account. Integration of Eq. (7.34a) (see Vol. 1, Sec. 7.12) within the limits from $p^{(b)}$ to $p^{(a)}$ gives

$$p^{(a)}-p^{(b)}=\Pi=-\frac{RT}{\bar{v}_1}\ln\frac{a_1^{(a)}}{a_1^{(b)}} \tag{21.21}$$

where $\bar{v}_1=\bar{v}_1^{(a)}=\bar{v}_1^{(b)}$ is the partial volume of the solvent in the solution. It does not depend on the pressure and composition of the solution.

Considering the passing of ions $Me^+$ and $A^-$ through the membrane in equilibrium, we must take into account the gradient of the electrical potential. In this case (in the absence of a pressure jump) we have equality not of the chemical potentials $\mu_i$, but of the electrochemical potentials $\bar{\mu}_i$ [see Vol. 1, Sec. 5.5, Eq. (5.14a)] for the ions passing through the membrane:

$$\bar{\mu}_+^{(a)}=\bar{\mu}_+^{(b)};\quad \bar{\mu}_-^{(a)}=\bar{\mu}_-^{(b)} \tag{21.22}$$

where

$$\bar{\mu}_+^{(a)} \equiv \mu_+^{(a)} + \psi^{(a)}F; \quad \bar{\mu}_-^{(a)} \equiv \mu_-^{(a)} - \psi^{(a)}F$$

$$\bar{\mu}_+^{(b)} \equiv \mu_+^{(b)} + \psi^{(b)}F; \quad \bar{\mu}_-^{(b)} \equiv \mu_-^{(b)} - \psi^{(b)}F$$

Taking account of the osmotic pressure, we get the conditions of equilibrium for the transfer of $dn_+$ cations or $dn_-$ anions:

$$\left.\begin{aligned} dA_+ &= \Pi\,\bar{v}_+\,dn_+ + [\bar{\mu}_+^{(a)} - \bar{\mu}_+^{(b)}]\,dn_+ = 0 \\ dA_- &= \Pi\,\bar{v}_-\,dn_- + [\bar{\mu}_-^{(a)} - \bar{\mu}_-^{(b)}]\,dn_- = 0 \end{aligned}\right\} \tag{21.23}$$

or, taking Eq. (21.22) into consideration and denoting $\psi^{(a)} - \psi^{(b)} = \varphi_m$ (the membrane potential)

$$\left.\begin{aligned} dA_+ &= \Pi\bar{v}_+\,dn_+ + [\mu_+^{(a)} - \mu_+^{(b)}]\,dn_+ + \varphi_m F\,dn_+ = 0 \\ dA_- &= \Pi\bar{v}_-\,dn_- + [\mu_-^{(a)} - \mu_-^{(b)}]\,dn_- - \varphi_m F\,dn_- = 0 \end{aligned}\right\} \tag{21.24}$$

or, finally, inserting into Eqs. (21.24) the expressions for the chemical potentials through the activities

$$\mu_+ = \mu_+^\circ + RT\ln a_+; \qquad \mu_- = \mu_-^\circ + RT\ln a_-$$

we get

$$\left.\begin{aligned} \Pi\bar{v}_+ + RT\ln\frac{a_+^{(a)}}{a_+^{(b)}} + \varphi_m F &= 0 \\ \Pi\bar{v}_- + RT\ln\frac{a_-^{(a)}}{a_-^{(b)}} - \varphi_m F &= 0 \end{aligned}\right\} \tag{21.25}$$

Summation of Eqs. (21.25) yields

$$\Pi(\bar{v}_+ + \bar{v}_-) + RT\ln\frac{a_+^{(a)}a_-^{(a)}}{a_+^{(b)}a_-^{(b)}} = 0 \tag{21.26}$$

Comparing this equation with Eq. (21.21) and deleting $\Pi$, we get

$$\ln\frac{a_+^{(a)}a_-^{(a)}}{a_+^{(b)}a_-^{(b)}}\,\frac{\bar{v}_1}{\bar{v}_+ + \bar{v}_-} = \ln\frac{a_1^{(a)}}{a_1^{(b)}}$$

or

$$\frac{a_+^{(a)}a_-^{(a)}}{a_+^{(b)}a_-^{(b)}} = \left[\frac{a_1^{(a)}}{a_1^{(b)}}\right]^{\frac{\bar{v}_1}{\bar{v}_+ + \bar{v}_-}} \tag{21.27}$$

Let us consider infinitely dilute solutions for which the activities equal the molalities, and $a_1^{(a)} \approx a_1^{(b)}$. In these conditions from Eq. (21.27) we find

$$m_+^{(a)}m_-^{(a)} = m_+^{(b)}m_-^{(b)} \tag{21.28}$$

Using the quantities characterizing equilibrium in part (*a*) of the system shown in Fig. 21.1 (diagram *II*), we get from Eq. (21.28)

$$(m_1 + x)\,x = (m_2 - x)^2$$

or

$$x = \frac{m_2^2}{m_1 + 2m_2} \tag{21.29}$$[1]

[1] The law of membrane equilibrium in the form of Eq. (21.29) was derived by Donnan (1911) and verified for solutions of congo red, where $R^-$ is $(C_{32}H_{22}N_6S_2O_6)^{2-}$.

If both solutions are infinitely dilute ones and $a_1^{(a)} = a_1^{(b)}$, the osmotic pressure of solution (*a*) relative to (*b*) should equal zero [see Eq. (21.21)]. At finite, though low concentrations, however, this equation, strictly speaking, is not observed. To find the osmotic pressure in a dilute solution, let us use in Eq. (21.21) activities of the solvent proportional to its mole fractions $x_1^{(a)}$ and $x_1^{(b)}$ [see. Vol 1, Sec. 6.8, Eq. (6.26a)]:

$$\frac{a_1^{(a)}}{a_1^{(b)}} \approx \frac{x_1^{(a)}}{x_1^{(b)}} \approx = \frac{\frac{1000}{M_1} + m_+^{(b)} + m_-^{(b)}}{\frac{1000}{M_1} + m_+^{(a)} + m_-^{(a)} + m_R^{(a)}} \tag{21.30}$$

where $m_R$ is the molality of the anion $R^-$.

Inserting the values of the molalities for parts (*a*) and (*b*) in diagram *II* of Fig. 21.1 and dividing the numerator and denominator of Eq. (21.30) by $1000/M_1$, we get

$$\frac{a_1^{(a)}}{a_1^{(b)}} \approx \frac{m_1^{(a)}}{m_1^{(b)}} = \frac{1 + \frac{2(m_2 - x)}{1000/M_1}}{1 + \frac{2(m_1 + x)}{1000/M_1}} = \frac{1 + C_2}{1 + C_1} \tag{21.31}$$

Returning to Eq. (21.21), we insert into it $a_1^{(a)}/a_1^{(b)}$ from Eq. (21.31), expand $\ln(1 + C_2)$ and $\ln(1 + C_1)$ into a series and limit ourselves to the first terms of the expansion:

$$\Pi = -\frac{RT}{\bar{v}_1} \ln \frac{1 + C_2}{1 + C_1} \approx -\frac{RT}{\bar{v}_1}(C_2 - C_1) = -\frac{RT}{\bar{v}_1} \frac{2(m_2 - x - m_1 - x)}{1000/M_1}$$

or

$$\Pi = -\frac{2RT}{1000} \frac{M_1}{\bar{v}_1} (m_2 - m_1 - 2x) \tag{21.32}$$

Let us insert into Eq. (21.32) for a dilute solution $M_1/\bar{v}_1 = \rho^\circ$ (the density of a pure solvent) and $x$ from Eq. (21.29). After transformation we get

$$\Pi = \frac{2RT\rho^\circ}{1000} \frac{(m_1 + m_2)\, m_1}{m_1 + 2m_2} \tag{21.33}$$

At values of $m_1$ and $m_2$ of the order of 0.001 for aqueous solutions ($\rho^\circ = 1$ g/cm$^3$, $R = 82.05$ cm$^3$·atm mol·K) we find $\Pi \approx 0.03$ atm $\approx 27$ mm Hg.

To find the equilibrium value of the membrane potential $\varphi_m$ in a dilute solution, we must return to Eqs. (21.25), equate the values of the activities $a_+$ and $a_-$ to the molalities $m_+$ and $m_-$ and insert the values of the molalities from diagram *II* of Fig. 21.1:

$$\left.\begin{aligned} \Pi\bar{v}_+ + RT \ln \frac{m_1 + x}{m_2 - x} + \varphi_m F = 0 \\ \Pi\bar{v}_- + RT \ln \frac{x}{m_2 - x} - \varphi_m F = 0 \end{aligned}\right\} \tag{21.34}$$

We insert the equilibrium value of $x$ [from Eq. (21.29)]:

$$\left.\begin{aligned} \Pi\bar{v}_+ + RT \ln \frac{m_1 + m_2}{m_2} + \varphi_m F = 0 \\ \Pi\bar{v}_- + RT \ln \frac{m_1 + m_2}{m_2} - \varphi_m F = 0 \end{aligned}\right\} \tag{21.35}$$

whence

$$\left.\begin{aligned}\varphi_m &= -\frac{RT}{F}\ln\frac{m_1+m_2}{m_2}-\frac{\Pi\bar{v}_+}{F}\\ \varphi_m &= -\frac{RT}{F}\ln\frac{m_1+m_2}{m_2}+\frac{\Pi\bar{v}_-}{F}\end{aligned}\right\} \qquad (21.36)$$

The first terms of the right-hand part of Eqs. (21.36) are equal. The second terms differ in value ($\bar{v}_+ \neq \bar{v}_-$) and in sign. This difference is due to simplifications in deducing the equilibrium value of $x$ according to Eq. (21.33) for a dilute solution and to the failure to take account of the mutual influence of the quantities $\Pi$ and $\varphi_m$. The term $\Pi\bar{v}_+/F$ (or $\Pi\bar{v}_-/F$) at $m_1 = m_2 = 0.001$ is very small. As we have found above, in this case $\Pi = 0.03$ atm. Let us assume that $\bar{v}_+ = \bar{v}_- = 0.05$ dm³. Since $F = 23\,060$ cal/V $= 920$ atm·dm³/V, then $\Pi\bar{v}_+/F = +0.03\times0.050/920 = 2\times10^{-6}$ V. The logarithmic terms of Eqs. (21.36) are equal to 0.156 V in our example.

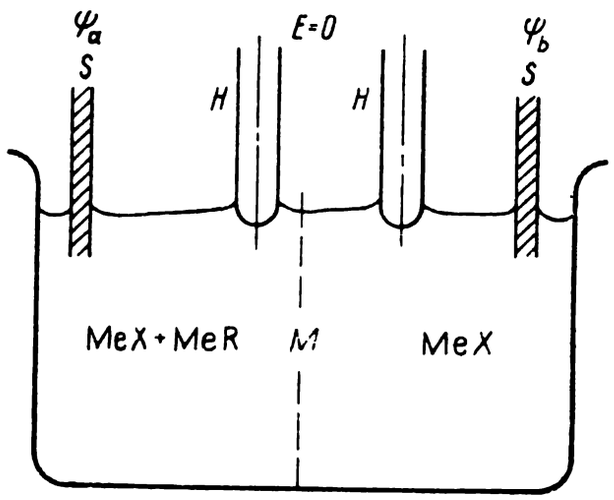



Fig. 21.2. Measuring of membrane potential:
*M*—membrane; *H*—hydrogen electrodes; *S*—salt bridges

Thus, the membrane potential difference in the simplest case (when the osmotic pressure can be neglected) is equal to the e.m.f. of a concentration cell relative to the cations or anions penetrating through the membrane.

If there are no special devices essential for creating and maintaining an osmotic pressure, then the term $\Pi\bar{v}/F$ in Eqs. (21.36) disappears. The potential jump across the membrane will be practically the same as in the presence of an osmotic pressure, for instance in the numerical example consid above. The system in this case not be in complete equilibrium, however, since the solvent in solutions (*a*) and (*b*) has different activities not compensated by the difference of pressures. The solvent will pass through the membrane from the right to the left, displacing ionic equilibrium.

Figure 21.2 shows an installation for measuring the membrane potential between solutions, where $X^- = Cl^-$. The letters *H* denote hydrogen electrodes immersed into solutions separated by membrane *M*. The difference of potentials of these electrodes being measured is equal to zero after membrane equilibrium is reached, while the actual potential difference is compensated by the membrane potential. The pair of electrodes *H* thus serves as an indicator that equilibrium has been reached between the left and right solutions (see Fig. 21.2) or between solutions (*a*) and (*b*) (see Fig. 21.1, diagram *II*) through the membrane. Identical calomel electrodes connected by salt bridges *S* to the two solutions where the concentrations of $Cl^-$ ($X^-$) are in the ratio $m_2/(m_1 + m_2)$ makes it possible to measure the e.m.f. of the concentration cell relative to $X^-$, i.e. the membrane potential $\varphi_m$ (see Eqs. 21.36).

Membrane equilibria have a great significance in investigating solutions of high polymers. In Vol. 1 (Sec. 7.14) we considered a method for determining the molecular mass of a high polymer by measuring the osmotic pressure of a solution. The laws set out there, however, are true only for solutions of substances that do not dissociate electrolytically, or for solutions free of ions of low-molecular substances. In the general case Eq. (21.28) should be used

and account also taken of the valence $z$ of the ion R. Introducing $z$, we get the following equations from Eq. (21.28) instead of Eq. (21.29):

$$x=\frac{m_2^2}{zm_1+2m_2}$$

$$\Pi=\frac{RT\rho^\circ}{1000}\,\frac{m_1\,[z\,(z+1)\,m_1+2m_2]}{zm_1+2m_2} \tag{21.37}$$

When $m_1 \gg m_2$ we get

$$\Pi=\frac{RT\rho^\circ}{1000}\,(z+1)\,m_1$$

When $m_1 \ll m_2$

$$\Pi=\frac{RT\rho^\circ}{1000}\,2m_1$$

The measured osmotic pressure in both extreme cases corresponds to the concentration of a high polymer. For this reason, knowing the osmotic pressure, we can determine the molecular mass of the high polymer (if $z$ is known).

Membrane equilibria are of considerable significance in the investigation of colloidal solutions in which a colloidal particle carrying a charge $z$ of one sign or the other plays the part of the ion R. Generally the laws that hold for infinitely dilute solutions cannot be applied to colloidal solutions even at great dilutions. Investigating the osmotic pressure and membrane potentials of colloidal solutions, we can determine the relation between the number of ions of opposite signs adsorbed on the surface of a colloidal particle and the concentration and nature of the ions in a solution

**21.6*. Glass Electrode.** In cells similar to cell *II* (see p. 536), the phenol solution can be replaced with a thin-walled glass membrane that contains ions $H^+$ and is sufficiently thin to have a certain electrical conductance which makes it possible to measure the e.m.f. of the cell.

No electrons participate in the reaction on the surface of the glass membrane, and the transfer of electricity across the boundary is ensured by the migration of $H^+$ (and other cations) from the liquid solution into the glass or vice versa. On both boundaries of the membrane with the solutions (surfaces ′ and ″) potential jumps set in that are determined by the composition of the glass and the solution:

$$\varphi'_{gl}=\varphi'^\circ_{gl}+\frac{RT}{F}\ln\frac{a'_{H^+}}{a'_{H^+gl}} \tag{21.38a}$$

$$\varphi''_{gl}=\varphi''^\circ_{gl}+\frac{RT}{F}\ln\frac{a''_{H^+}}{a''_{H^+gl}} \tag{21.38b}$$

The difference between the potential jumps on the surface of a membrane is called the *potential of a glass electrode* ($\varphi_{gl}$)

$$\varphi'_{gl}-\varphi''_{gl}=\varphi_{gl}=\varphi'^\circ-\varphi''^\circ+\frac{RT}{F}\ln\frac{a''_{H^+gl}}{a'_{H^+gl}}+\frac{RT}{F}\ln\frac{a'_{H^+}}{a''_{H^+}} \tag{21.39}$$

The surfaces of a glass membrane are not quite identical (especially in connection with their curvature). Even upon equality of the activities of the hydrogen ions in the solutions at both sides of the membrane ($a''_{H^+}=a'_{H^+}$) and, apparently, also when $a''_{Hg^+gl}=a'_{H^+gl}$ the quantity $\varphi_{gl}$ is not equal to zero. Thus

$$\varphi'^\circ-\varphi''^\circ+\frac{RT}{F}\ln\frac{a''_{H^+gl}}{a'_{H^+gl}}=\varphi_{as}\neq 0$$

The quantity $\varphi_{as}$ is called the *asymmetry potential.*

The hydrogen ions in the solution and the ions of metals, especially alkaline ones, in the glass are capable of entering into an exchange reaction:

$$H^+_{gl} + Me^+ = H^+ + Me^+_{gl}$$

The equilibrium constant of this exchange

$$K_{exch} = \frac{a_{H^+} a_{Me^+gl}}{a_{H^+gl} a_{Me^+}}$$

is usually very great[1], namely, $K_{exch} = 10^{10}\text{-}10^{14}$.

Since the ions $H^+$ and $Me^+$ in the glass substitute each other, we can consider as a first assumption that

$$a_{H^+gl} + a_{Me^+gl} = \text{const} = a$$

where $a$ is a constant for glass of a given composition.

Hence

$$K_{exch} = \frac{a_{H^+}(a - a_{H^+gl})}{a_{H^+gl} a_{Me^+}} \tag{21.40}$$

Let us solve Eq. (21.40) with respect to $a_{H^+gl}$:

$$a_{H^+gl} = \frac{K_{exch} a a_{H^+}}{K_{exch} a_{H^+} + a_{Me^+}} = \frac{a a_{H^+}}{a_{H^+} + \dfrac{a_{Me^+}}{K_{exch}}}$$

Dividing both parts of this equation by $a_{H^+}$, inverting the ratio obtained and inserting the ratio $\dfrac{a_{H^+}}{a_{H^+gl}}$ into Eqs. (21.38) we get

$$\varphi'_{gl} = \varphi'^{\circ}_{gl} + \frac{RT}{F} \ln \frac{a'_{H^+} + \dfrac{a'_{Me^+}}{K_{exch}}}{a} \tag{21.41}$$

and the same for the solution $''$.

It is obvious that in acid and weakly alkaline solutions

$$a_{H^+} \gg \frac{a_{Me^+}}{K_{exch}}$$

and the surface of the glass membrane functions like a hydrogen electrode:

$$\left.\begin{aligned} \varphi'_{gl} &= \varphi'^{\circ}_{gl} - \frac{RT}{F} \ln a + \frac{RT}{F} \ln a'_{H^+} = A' + B' \ln a'_{H^+} \\ \varphi''_{gl} &= \varphi''^{\circ}_{gl} - \frac{RT}{F} \ln a + \frac{RT}{F} \ln a''_{H^+} = A'' + B'' \ln a''_{H^+} \end{aligned}\right\} \tag{21.42}$$

Determining the difference between the potential jumps on the two surfaces of a glass electrode $\varphi_{gl} = \varphi'_{gl} - \varphi''_{gl}$ (the potential of the glass electrode), we can use Eqs. (21.42) to find $a'_{H^+}/a''_{H^+}$ in the two solutions at both sides of the mem-

[1] The values of $K_{exch}$ vary quite considerably for different kinds of glass, from $10^3$ for alimina-silicate glass (pH $\geqslant$ 3) up to $10^{16}$ for certain silicate glasses. This makes it possible to measure the pH in alkaline solutions up to the normal concentration.

brane. If $a''_{H^+}$ is known, we can thus find the unknown quantity $a'_{H^+}$ in the solution being investigated. The quantity $A = A' - A''$ in Eqs. (21.42) is found by calibration of the glass electrode according to a solution with a known value of $a_{H^+}$.

For strongly alkaline solutions (pH > 12) we have $a_{H^+} < a_{Me^+}/K_{exch}$ and Eq. (21.41) becomes

$$\varphi'_{gl} = A' + \frac{RT}{F} \ln \frac{a_{Me^+}}{K_{exch}} = C' + \frac{RT}{F} \ln a_{Me^+}$$

If the ion $Me^+$ is a cation in a solution of an alkali, then

$$a_{Me^+} \approx a_{OH^-} = \frac{K_w}{a_{H^+}}$$

where $K_w$ is the ionic product of water.

Hence

$$\varphi'_{gl} = C' + \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln a_{H^+} = D' - B \ln a_{H^+} \qquad (21.43)$$

i.e. in this region too the quantity $\varphi_{gl}$ is a logarithmic function of the activity of the ions $H^+$ of the solution with a coefficient having the reverse sign. A more

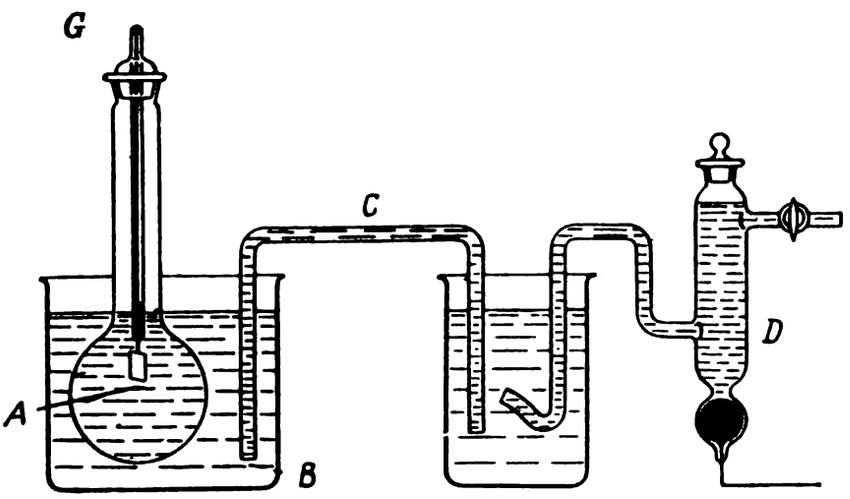



Fig. 21.3. Cell with glass electrodes:

*A*—glass electrode; *B*—vessel; *C*—salt bridge; *D*—reference electrode; *G*—silver-silver chloride electrode

complete consideration of the e.m.f. of cells with a glass electrode requires inclusion of the diffusion potentials in the surface layers of the glass. In the simplest cases this leads to replacement of $K_{exch}$ by the product $K_{exch}(U_{H^+}/U_{Me^+})$, where $U$ is the mobility of the ions.

Figure 21.3 shows a cell in which a glass electrode (flask with solution $A$) is used to measure the activity of $H^+$ in solution $B$ ($a_{H^+x}$). Flask $A$ contains a solution of a definite composition into which an electrode, for example a silver-silver chloride one $G$, is immersed. The cell is provided with salt bridge $C$ and reference electrode $D$, for example a calomel one. The e.m.f. of the entire cell is the sum of the electrode potentials: $\varphi_{AgCl}$—of the silver-silver chloride electrode, $\varphi_{gl} = \varphi'_{gl} - \varphi''_{gl}$—of the glass electrode, and $\varphi_{Hg_2Cl_2}$—of the calomel electrode. The potentials $\varphi_{AgCl}$, $\varphi'_{gl}$ (on the inner wall of flask $A$) and $\varphi_{Hg_2Cl_2}$

are constant (for the given solutions in flask $A$ and half-cell $D$), while $\varphi''_{gl}$ (on the external wall of flask $A$) is related to $a_{H^+}$ by Eq. (21.42).

Thus

$$E=(\varphi_{AgCl}+\varphi'_{gl}+\varphi_{Hg_2Cl_2}+\varphi''^{\circ}_{gl})+\frac{RT}{F}\ln a_{H^+x}=E_{gl}+\frac{RT}{F}\ln a_{H^+x}$$

The value of $E_{gl}$ is established by calibration for a specific cell with definite electrode $C$, solution $A$ and half-cell $D$.

The theory of the glass electrode set out above was developed by B. Nikolsky and his school.

The glass electrode is widely used for determining the pH of solutions, especially if the solutions being investigated contain strong oxidizers, reducers or substances poisoning metal electrodes.

Since the resistance of a glass electrode is very high, the current flowing in the cell is very small. This is why instruments that do not practically consume current are used as a null-instrument. They include electrometers and electrical circuits with valve amplifiers.

CHAPTER 22

# E.M.F. MEASUREMENT AS A METHOD OF PHYSICOCHEMICAL RESEARCH

**22.1. E.M.F. and Activity Coefficients of Electrolytes.** Measurement of the e.m.f.s of various electrochemical cells is a convenient method for the experimental evaluation of the activity coefficients of separate salts in solutions having a complicated composition, and for studying the mutual influence of the components of such electrolytes on their activities. Cell without transference (b) (Sec. 21.2, p. 529) can serve as an example.

Here the dissolved acid HCl is transferred from solution $'$ to solution $''$ not directly, but as a result of two oppositely directed electrochemical reactions. Owing to the absence of diffusion potentials, such cells make it possible to exactly determine the activity coefficient of a definite component (in the given case HCl in the electrolyte, whose composition may be made more complicated).

To find $a_\pm$ it is necessary to use the limiting condition according to which $a_\pm \to m_\pm$ at $m \to 0$ or, which is the same, $\gamma_\pm \to 1$ at $m \to 0$. Let us assume for simplicity that $z_+ = z_- = 1$ and $m_\pm = m$. Let us measure the e.m.f. in a series of cells for which $m'$ and, therefore, $a'_\pm$ are constant quantities, and $m''$ and $a''_\pm$ systematically decrease. Transforming Eq. (21.2) in such a way as to gather measureable quantities ($E$ and $m''$) in the left-hand part and inserting $a''_\pm = m''\gamma''_\pm$, we get

$$E + \frac{2RT}{F} \ln m'' = \frac{2RT}{F} \ln a'_\pm - \frac{2RT}{F} \ln \gamma''_\pm \qquad (22.1)$$

As the value of $m''$ decreases, that of $\ln \gamma''_\pm$ approaches zero. Hence, at $m'' \to 0$

$$\lim \left( E + \frac{2RT}{F} \ln m'' \right) = \frac{2RT}{F} \ln a'_\pm \qquad (22.2)$$

at 25 °C

$$\lim (E + 0.1183 \log m'') = 0.1183 \log a'_\pm \qquad (22.2a)$$

To find $a'_\pm$ it is necessary to graphically extrapolate the quantity in parentheses as a function of $m$ when $m \to 0$. It is convenient to make use of the fact that at low concentrations the value of $\log \gamma''_\pm$ depends linearly on $m^{1/2}$ [in the more general case, in mixtures of electrolytes, on $I^{1/2}$, where $I$ is the ionic strength (see Sec. 16.7)]. Hence, when

depicting graphically $E + 0.1183 \log m''$ versus $(m'')^{1/2}$, at sufficiently low values of $m$ we get a straight line that is easily extrapolated to $m \to 0$. This allows us to determine the value of $a'_{\pm}$ for an electrolyte of a constant composition.

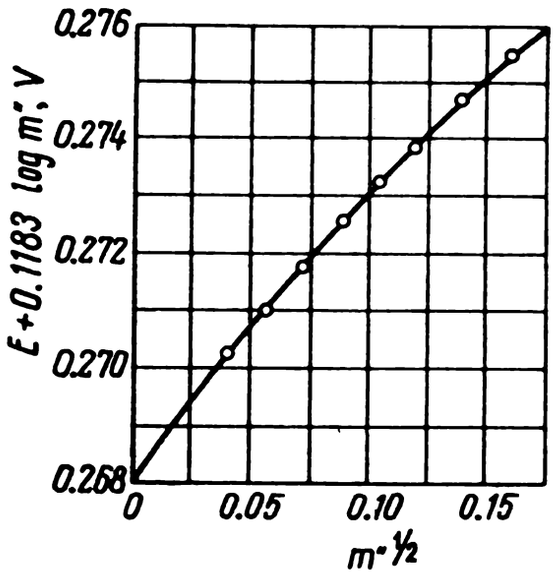



Fig. 22.1. Graphical extrapolation when finding the activity coefficient by the e.m.f. method

Knowing $\log a'_{\pm}$ from Eq. (22.2a) and, therefore, $\ln a'_{\pm}$, we can use Eq. (22.1) to find $\ln \gamma'_{\pm}$ for any solution within the interval of concentrations investigated according to the measured values of $E$ and $m''$.

Figure 22.1 shows a way of finding $a'_{\pm}$ by extrapolation of the data for a cell with HCl, aq similar to the one considered above, but in which a calomel electrode was used instead of the silver-silver chloride one.

A glance at Fig. 22.1 shows that the value of the left-hand part of Eq. (22.2) determined by extrapolation of the curve is equal to $0.2680 = 0.1183 \times \times \log a'_{\pm}$ for a solution of HCl having a constant concentration. Using this value instead of the first term of the right-hand part of Eq. (22.1), we can compute the activity coefficient $\gamma''_{\pm}$ for a solution of HCl of any concentration within the range of concentrations being studied:

$$0.1183 \log \gamma''_{\pm} = 0.2680 - (E + 0.1183 \log m'') \qquad (22.1a)$$

Thus, when $m'' = 0.0225$ $[(m'')^{1/2} = 0.15]$, the sum $E + 0.1183 \times \times \log m''$ is equal to 0.2752. Inserting this value into Eq. (22.1a), we find

$$\log \gamma''_{\pm} = \frac{0.2680 - 0.2752}{0.1183} = -0.0601$$

The sought quantity $\gamma''_{\pm} = 0.871$ and $a''_{\pm} = \gamma''_{\pm} m''_{\pm} = 0.0196$. If $z_+$ and $z_-$ do not equal unity, then, using Eq. (21.2a), we get for 25 °C

$$\lim \left(E + \frac{z_+ + z_-}{z_+ z_-} 0.0591 \log m''\right) = \frac{z_+ + z_-}{z_+ z_-} 0.0591 \log a'_{\pm} \qquad (22.2b)$$

It follows from the calculation given above that a chart similar to the one in Fig. 22.1 allows us to compute $\gamma''_{\pm}$ without knowing the molality of the solution of constant composition used in the series of measurements necessary for plotting the curve.

To measure the activity coefficients of solutions of alkali metal compounds (NaCl, $K_2SO_4$, LiOH, etc.) by this method, the hydrogen electrode has to be replaced with an electrode of alkali metal amal-

gams. The latter is taken in combination with a silver or mercury electrode in saturated solutions of the corresponding compounds of silver (AgCl, $Ag_2SO_4$ or $Ag_2O$) or mercury.

This method (with the use of concentration cells without transference) is very convenient for studying the influence of various salts on the activity coefficient of a salt being investigated.

**22.2*. E.M.F. and Transport Numbers of Ions.** A concentration cell with transference can be used to measure the transport number as a function of the concentration. As already shown in Sec. 21.3, the effect of operating a concentration cell with transference (in the simplest case of identical mono-monovalent electrolytes) is to transfer $t_-$ gramme-equivalents of a salt from one solution to the other through a diffuse layer. A diagram of the transference of the solute in a narrow zone inside the diffuse layer is shown below

$$\mathrm{H_2} \mid \underset{m'}{\mathrm{HCl}} \quad \overset{t_- + dt_-}{\longrightarrow} \; a \;\vdots\; \underset{m+dm}{} \quad \overset{t_-}{\longrightarrow} \; \underset{m}{\vdots\; b} \;\Big|\; \underset{m''}{\mathrm{HCl}} \mid \mathrm{H_2}$$

$$m' > m''$$

When one faraday of electricity passed through layer $ab$, $t_- + dt_-$ g-eq of the salt appeared in it and $t_-$ disappeared, i.e. there appeared $dt_-$ g-eq of the salt at a concentration $m$ and a chemical potential $\mu$. Therefore the change in the Gibbs energy $dG$ of the solution connected with the change of the mass of the salt in this layer is

$$dG = \mu dt_-$$

The total change in $G$ in the entire cell will consist of the changes in the two electrolytes (without taking the diffuse layer into account)

$$\Delta G_1 = -t'_-\mu' + t''_-\mu''$$

and of the change in $G$ in the diffuse layer (we integrate in the direction of the growth of $t_-$):

$$\Delta G_2 = \int_{t''_-}^{t'_-} \mu\, dt_- = -\int_{t'_-}^{t''_-} \mu\, dt_-$$

The total change in $G$ is equal to $-FE$:

$$-FE = \Delta G = \Delta G_1 + \Delta G_2 = -t'_-\mu' + t''_-\mu'' - \int_{t'_-}^{t''_-} \mu\, dt_- = +\int_{\mu'}^{\mu''} t_-\, d\mu$$

Since for the dissolved salt we have $d\mu = 2RT\, d \ln a_\pm$, then

$$E = -\frac{2RT}{F} \int_{a'_\pm}^{a''_\pm} t_- d \ln a_\pm \tag{22.3}$$

We finally get

$$t_- = -\frac{E}{2RT}\left(\frac{\partial E}{\partial \ln a_\pm}\right) \tag{22.4}$$

Having studied the activities $a_{\pm}$ with the aid of cells without transference and obtained an experimental curve $E = f(\ln a_{\pm})$ for a concentration cell with transference in which one of the concentrations remains constant, by graphical differentiation we get values of $t_- = f(a_{\pm}) = f(m)$. If the dependence $t_- = f(m)$ is known from data obtained in other ways, then we can use the e.m.f.s of cells with transference to determine the activity by solving Eq. (22.4) with respect to $d\ln a_{\pm}$ and integrating with respect to $E$. It should be noted that the e.m.f. method can be used to find only the *apparent transport numbers* (*Hittorf numbers*), and not the *true transport numbers*.

**22.3. Concentration Cells with Electrodes Formed by Variable Concentration Metal Solutions. Measuring Activity of an Electrode Component.** An example of a cell with electrodes formed by solutions of variable concentration is the cell

$$(-)\,\mathrm{Hg+Zn}\,\Big|_{m''}\,\mathrm{ZnSO_4}\,\Big|_{m'}\,\mathrm{Zn+Hg}\,(+)$$

in which the transfer of zinc from the amalgam with the higher concentration $m''$ to the one with the lower concentration $m'$ is the current-forming process:

$$E = -\frac{\Delta G}{zF} = -\frac{RT}{zF}\ln\frac{a'}{a''} \tag{22.5}$$

At low concentrations of the zinc in the amalgams we have $a \approx m$, in accordance with the second method of selecting the standard state [Vol. 1, Sec. 6.8, Eq. (6.30)]. The value of $E$ calculated by the equation

$$E = -\frac{RT}{zF}\ln\frac{m'}{m''} \tag{22.6}$$

coincides with experimental values at $m < 0.004$. The deviations at greater values of $m$ make it possible to calculate the activity of the zinc in the amalgam.

At high temperatures, the e.m.f.s of concentration cells in which the electrodes are metal melts or solid solutions and the space between them is filled with a salt melt can be measured.

For example

$$\begin{array}{r|c|l} (-\mathrm{Pb}) & \mathrm{KCl+NaCl+PbCl_2} & \mathrm{Bi+Pb}\,(+) \\ (\mathrm{lq}) & (\mathrm{lq}) & (\mathrm{lq}) \\ a_{\mathrm{Pb}}=1 & & a_{\mathrm{Pb}}<1 \end{array}$$

The current-forming process consists in the transition of lead from the molten left electrode (pure lead) to the molten right electrode (a melt of lead and bismuth), i.e. to solution of the molten lead in the melt. The measured e.m.f. of such a cell obviously makes

it possible to calculate the activity of the lead in the melt:

$$E = -\frac{RT}{zF} \ln a_{Pb}$$

A cell with two hydrogen electrodes having different pressures of the hydrogen, which allows us to study deviations of the behaviour of $H_2$ from the laws of ideal gases, and also to determine the concentration of hydrogen in a complex gas mixture, was already considered [Sec. 21.2, Eq. (21.4)].

**22.4. Calculation of Oxidation-Reduction Equilibria in Solutions Using Tables of Standard Electrode Potentials.** In Sec. 20.9 we considered electrodes of a noble metal that exchange electrons with ions of a variable valence in a solution ($Fe^{2+} \rightarrow Fe^{3+} + e$, $Sn^{4+} + 2e \rightarrow Sn^{2+}$, etc.). A definite oxidation-reduction potential sets in on the electrode.

Let us consider a method of calculating the equilibria of ionic oxidation-reduction reactions in a solution. If we want to find the direction of the reaction $Fe^{2+} + Cr^{3+} \rightleftarrows Fe^{3+} + Cr^{2+}$, we prepare a cell with two oxidation-reduction electrodes. In the first approximation we use the standard potentials of these electrodes from Table 20.2. For the left electrode we take the value of its standard potential $E^\circ$ with the sign given in the table, and for the right electrode its standard potential with the reverse sign. If the sum of the electrode potentials (the cell e.m.f.) taken in this manner is positive, the current flows from the right to the left in the cell (the direction is indicated in accordance with the notation used to symbolize the cell). An oxidation process proceeds at the right electrode and a reduction process at the left one. If the e.m.f. of the cell is negative, the current in it flows from the left to the right, i.e. the reverse reaction proceeds.

For more accurate calculation of the direction of a process in the general case (the electrodes are not standard), account must be taken of the activity of the ions in the solutions.

It is quite obvious that the results of calculating the direction of oxidation-reduction reactions and their electrochemical equilibria in cells may be applied to the same reactions proceeding with direct mixing of the solutions containing different ions. Let us consider several examples.

For the cell

$$\underset{\varphi_1}{(-)\,Pt \mid Sn^{2+},\ Sn^{4+} \parallel Fe^{2+},\ Fe^{3+} \mid Pt\,(+)}\ \varphi_2$$

by Eq. (20.28) we get

$$E = \varphi_2 - \varphi_1 = \varphi_2^\circ - \varphi_1^\circ - \frac{RT}{2F} \ln \frac{a^2_{Fe^{2+}} a_{Sn^{4+}}}{a_{Sn^{2+}} a^2_{Fe^{3+}}}$$

Taking the values of $\varphi_1^\circ$ and $\varphi_2^\circ$ from Table 20.2, we get

$$E^\circ = \varphi_2^\circ - \varphi_1^\circ = 0.771 - 0.150 = 0.621 \text{ V}$$

$$E = \varphi_2 - \varphi_1 = 0.621 - 0.029 \log \frac{a^2_{Fe^{2+}} a_{Sn^{4+}}}{a_{Sn^{2+}} a^2_{Fe^{3+}}} \qquad (22.7)$$

If the concentrations of the ions in the numerator are not negligibly small, then the value of $E^\circ$ is greater than the logarithmic term, and the e.m.f. of the cell is positive, i.e. the current flows from the right to the left in the cell and the following reaction proceeds:

$$Sn^{2+} + 2Fe^{3+} = Sn^{4+} + 2Fe^{2+}$$

It is interesting to find the conditions of equilibrium of this reaction at which, obviously, the potentials of the electrodes are the same and the e.m.f. of the cell is equal to zero:

$$E = 0, \quad E^\circ = 0\ 621 = 0.029 \log \frac{a_{Sn^{4+}} a^2_{Fe^{2+}}}{a_{Sn^{2+}} a^2_{Fe^{3+}}}$$

The product of the activities after the logarithm symbol is the equilibrium constant. It is constant at a given temperature. There is evidently a multitude of partial solutions. Assuming, in a particular case, that the ratio of the activities of the ions $Fe^{2+}$ and $Fe^{3+}$ is equal to unity, we find

$$\log \frac{a_{Sn^{4+}}}{a_{Sn^{2+}}} = \frac{0.621}{0.029} \approx 21 \quad \text{and} \quad \frac{a_{Sn^{4+}}}{a_{Sn^{2+}}} = 10^{21}$$

If $a_{Sn^{4+}} = 1$ (this is a concentrated solution), then $a_{Sn^{2+}} = m_{Sn^{2+}} = 10^{-21}$ mol/dm$^3$. It is naturally impossible to obtain such a concentration and keep it constant.

Considering another particular case when $a_{Sn^{4+}}/a_{Sn^{2+}} = 1$, we get

$$\log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} = \left(\frac{0.621}{0.029}\right)^{1/2} \approx 4.6$$

i.e. $a_{Fe^{3+}} = 10^{-4.6}$ at $a_{Fe^{2+}} = 1$.

Low concentrations of such an order can be obtained and even kept constant if we use solutions containing complex ions with trivalent iron that weakly dissociate and give low concentrations of the free ions $Fe^{3+}$

**22.5. Equilibria of the Kind $2Me^+ = Me + Me^{2+}$.** For a metal giving ions of a different valence, for example $Cu^+$ and $Cu^{2+}$, we

can find the potentials $\varphi_I[Cu^+, aq \mid Cu]$ and $\varphi_{II}[Cu^{2+}, aq \mid Cu]$, and also the potential $\varphi_{III}[Cu^{2+}, Cu^+, aq \mid Cu]$. The relation between the values of these potentials can be found by multiplying them by $-zF$, as a result of which we get the changes in the Gibbs energy for the corresponding electrochemical processes:

$$-\varphi_I F = \Delta G_I; \qquad Cu^+ + e = Cu \qquad (I)$$

$$-2\varphi_{II} F = \Delta G_{II}; \qquad Cu^{2+} + 2e = Cu \qquad (II)$$

$$-\varphi_{III} F = \Delta G_{III}; \qquad Cu^{2+} + e = Cu^+ \qquad (III = II - I)$$

Since I + III = II, we have $\Delta G_I^\circ + \Delta G_{III}^\circ = \Delta G_{II}^\circ$ and $\varphi_I^\circ + \varphi_{III}^\circ = 2\varphi_{II}^\circ$. The standard values for II and III are $\varphi_{II}^\circ = 0.337$ V and $\varphi_{III}^\circ = 0.153$ V, whence $\varphi_I^\circ = 2\varphi_{II}^\circ - \varphi_{III}^\circ = 0.521$ V.

If metallic copper is in contact with a solution containing the ions $Cu^+$ and $Cu^{2+}$ and is in equilibrium with it, then the potential of the copper electrode should obey equations of type (20.14) for reactions I and II simultaneously:

$$\varphi_I = \varphi_I^\circ + \frac{RT}{F} \ln a_{Cu^+} = \varphi_{II} = \varphi_{II}^\circ + \frac{RT}{2F} \ln a_{Cu^{2+}} \qquad (22.8)$$

Multiplying both parts of the equation by two, we get

$$2\varphi_I^\circ + \frac{RT}{F} \ln a_{Cu^+}^2 = 2\varphi_{II}^\circ + \frac{RT}{F} \ln a_{Cu^{2+}}$$

whence

$$\ln \frac{a_{Cu^+}^2}{a_{Cu^{2+}}} = \frac{(\varphi_{II}^\circ - \varphi_I^\circ) F \times 2}{RT} \qquad (22.9)$$

Inserting the values of $\varphi_{II}^\circ$ and $\varphi_I^\circ$ from Table 20.1, we have

$$\log \frac{a_{Cu^+}^2}{a_{Cu^{2+}}} = \frac{(0.337 - 0.521) \times 23\,061 \times 2}{4.575 \times 298} = -6.219$$

and

$$\frac{a_{Cu^+}^2}{a_{Cu^{2+}}} = 6.04 \times 10^{-7}$$

The calculation for mercury ions is similar. From Table 20.1 we find the standard potentials of the electrodes

$$Hg^{2+} \mid Hg; \quad \varphi_I^\circ = 0.854 \text{ V}; \quad Hg^{2+} + 2e = Hg \qquad (I)$$

$$Hg_2^{2+} \mid Hg; \quad \varphi_{II}^\circ = 0.789 \text{ V}; \quad Hg_2^{2+} + 2e = 2Hg \qquad (II)$$

Comparing these reactions, we obtain

$$Hg^{2+}, Hg_2^{2+} \mid Hg; \quad \varphi_{III}^\circ = 0.065; \quad Hg_2^{2+} = Hg + Hg^{2+} \quad (III = I - II)$$

A mercury electrode in electrochemical equilibrium with a solution containing the ions $Hg_2^{2+}$ and $Hg^{2+}$ should have the same potential relative to both species

of mercury ions.

$$\varphi_{I}=\varphi_{II}\,;\quad \varphi_{I}^{\circ}+\frac{RT}{2F}\ln a_{Hg^{2+}}=\varphi_{II}^{\circ}+\frac{RT}{2F}\ln a_{Hg_2^{2+}}$$

$$\log\frac{a_{Hg_2^{2+}}}{a_{Hg^{2+}}}=\frac{(\varphi_{I}^{\circ}-\varphi_{II}^{\circ})\,2F}{RT}\,;\quad \log\frac{a_{Hg_2^{2+}}}{a_{Hg^{2+}}}=\frac{0.065\times 2\times 23\,060}{4.576\times 298}=2.20;\quad \frac{a_{Hg_2^{2+}}}{a_{Hg^{2+}}}=158$$

Thus, the equilibrium $Hg + Hg^{2+} = Hg_2^{2+}$ is shifted to the right and the concentration of the ions $Hg^{2+}$ is about 1% of the concentration of $Hg_2^{2+}$.

We get the same result when we use the value of $\varphi_{III}^{\circ} = 0.065$ V calculated above. This is the standard potential of the electrode $Hg_2^{2+}$, $Hg^{2+}$ | Hg. Such an electrode can obviously not exist, since the reaction will proceed in the direction of reduction of the potential until the latter becomes equal to zero. In this case

$$0=\varphi_{III}=\varphi_{III}^{\circ}+RT\ln\frac{a_{Hg_2^{2+}}}{a_{Hg^{2+}}}$$

and we arrive at the result already obtained above for the equilibrium $Hg + Hg^{2+} = Hg_2^{2+}$.

**22.6. Determining the pH of a Solution.** Some information on the pH was given in Sec. 18.10. Here we shall consider the potentiometric method of determining the pH. The latter is frequently defined as the common logarithm of the hydrogen ion concentration taken with the reverse sign, namely,

$$pH=-\log[H^+]\quad\text{and}\quad [H^+]=10^{-pH}$$

For solutions whose concentration is not very small it is more proper to take the activity of the hydrogen ions instead of $[H^+]$. In this case the $pH_a$ value for a solution should be defined as the common logarithm of the hydrogen ion activity in this solution with the reverse sign, namely,

$$pH_a=-\log a_{H^+}$$

It is very simple to measure the $pH_a$ value by the potentiometric method. If we introduce a small amount of quinhydrone into the solution whose $pH_a$ value is to be determined and immerse a platinum wire into the solution, we obtain a quinhydrone electrode. The e.m.f. of the cell formed by this electrode and a standard calomel one should be measured.

The e.m.f. of a cell consisting of a standard hydrogen and a standard quinhydrone electrodes at 25 °C is 0.699 V, and the potential of a calomel electrode relative to a hydrogen one is 0.244 V:

| Pt, $H_2$ | Calomel electrode | Quinhydrone electrode | Quinhydrone electrode |
|---|---|---|---|
| $a_{H^+}=1$ | | $a=a_x$ | $a_{H^+}=1$ |
| 0.244 | $E_m$ | | $E_x$ |

0.699

As follows from the diagram, $0.699 - (E_m + 0.244) = 0.455 - E_m = E_x$, where $E_m$ is the e.m.f. of the quinhydrone electrode that must be measured.

Hence

$$-\log a_{H^+} = pH_a = \frac{0.455 - E_m}{0.059} \text{ (at 25 °C)}$$

The method described above is simple and can be used in any laboratory. The errors in determining the $pH_a$ value by this method are very great, however. This is due to the presence of a diffusion potential and to the necessity of determining the pH of standard solutions. In the majority of cases buffer solutions (see Sec. 18.12) are of interest for practical purposes. A value of the activity of $H^+$ in a standard solution can be determined unambiguously by extrapolation of data for a solution of a strong acid to infinite dilution. But such a solution has a negligible buffer index and cannot serve as a standard.

The error of the method can be reduced if for determining the $pH_a$ value of a series of buffer solutions that can then serve as standards we use a cell without diffusion potentials (a cell without transference) consisting of two reversible electrodes of the first and second kinds, for example

$$\text{Pt, } H_2 \left| \begin{array}{c} \text{Buffer solution} \\ \text{containing } H^+ \text{ and} \\ Cl^- \end{array} \right| \text{AgCl, Ag}$$

Here

$$2 \log a_{\pm} = \log a_{H^+} m_{Cl^-} + \log \gamma_{Cl^-} = -\frac{E - E_0}{2.303RT}$$

The value of $\log a_{H^+}$ can be determined if we make some reasonable assumptions with respect to $\gamma_{Cl^-}$. This method makes it possible to determine the $pH_a$ value of standard solutions with an accuracy up to $\pm 0.01$ unit of $pH_a$ at low ionic strengths and up to $\pm 0.05$ for more concentrated solutions.

A set of standard solutions makes it possible to determine the $pH_a$ value with a formal accuracy up to $\pm 0.02$ unit (this is the accuracy required by the relevant USSR State Standard), but this is an instrumental accuracy having no direct physical meaning.

In practice, cells with transference and standard solutions are used for determining the $pH_a$ value.

Owing to the presence of diffusion potentials, however, it is rarely possible to determine the $pH_a$ value with an error less than $\pm 0.1$, and in more difficult cases less than $\pm 0.2$ unit of the $pH_a$ value.

**22.7. Solubility Product.** The solubility of sparingly soluble salts in solutions of other salts can be accurately determined by measur-

ing the e.m.f. of cells of the kind

$$(-)\,Ag\,|\,AgCl\,(s),\quad \underset{m_1}{MCl}\,|\,Cl_2,\quad Pt\,(+) \qquad (I)$$

(where M is H or a cation), in which the following reaction proceeds:

$$\frac{1}{2}Cl_2 + Ag\,(s) = AgCl\,(s)$$

and the e.m.f. can be compared with the concentration of the electrolyte:

$$E = \varphi^\circ_{Cl} - \frac{RT}{F}\ln a_{Cl^-} - \left(\varphi^\circ_{Ag} + \frac{RT}{F}\ln a_{Ag^+}\right) =$$

$$= \varphi^\circ_{Cl} - \varphi^\circ_{Ag} - \frac{RT}{F}\ln a_{Ag^+}a_{Cl^-} = \varphi^\circ_{Cl} - \varphi^\circ_{Ag} - \frac{RT}{F}\ln K_{ap,\,AgCl} \qquad (22.10)$$

where $a_{Ag^+}a_{Cl^-} = K_{ap,\,AgCl}$—the activity product of AgCl—is a constant quantity in a saturated solution and is equal to the activity of the solid salt AgCl[1].

From the table of standard potentials (Table 20.1) we find

$$\varphi^\circ_{Cl} = 1.358\,V \quad \text{and} \quad \varphi^\circ_{Ag} = 0.799\,V \text{ at } 25\,^\circ C$$

The measured value of $E = 1.136$ V. Hence

$$1.136 = 1.358 - 0.799 - 0.0591 \log K_{ap,\,AgCl}$$

whence

$$K_{ap,\,AgCl} = \gamma_\pm^2 m_{Ag^+}m_{Cl^-} = 1.77 \times 10^{-10}$$

Since the quantity $K_{ap,\,AgCl}$ is constant at a given temperature, and in a solution of AgCl in pure water $\gamma_\pm = 1$ (the solution is greatly diluted), then the solubility product for AgCl in pure water

$$K_{sp,\,AgCl} = m_{Ag^+}m_{Cl^-} = 1.77 \times 10^{-10}$$

and the solubility of AgCl in pure water is $\sqrt{K_{sp}} = 1.33 \times 10^{-5}$.

It is far from being always possible to prepare a cell for which the value of $K_{sp}$ for a separate salt is determined directly.

Generally only one of the two ions of the salt being investigated participates in a summary electrochemical process or in an electrode process. It becomes necessary to use a conventional assumption on the activity of one of the ions to calculate the value of $K_{sp}$ for this salt. Let us consider an example.

The potential of a silver-silver chloride electrode is measured relative to a calomel or hydrogen one with a reduction of the diffu-

[1] It should be remembered that the activities of a component in two phases in equilibrium are equal if the same standard state has been selected for both phases. The activity of a separate solid, like its chemical potential, is constant at a constant pressure and temperature.

sion potential to a minimum:

$$(-)\,Hg\,|\,Hg_2Cl_2\,(s)\,;\quad \underset{m=0.1}{MeCl}\,\|\,\underset{m=0.1}{MeCl}\,;\quad AgCl\,(s)\,|\,Ag\,(+) \qquad \text{(II)}$$

Having found the potential of the silver-silver chloride electrode relative to a standard hydrogen one, we apply to the former electrode the Nernst equation:

$$\varphi_{Ag,\,AgCl} = \overset{\circ}{\varphi}_{Ag} + \frac{RT}{F}\ln a_{Ag^+} = \overset{\circ}{\varphi}_{Ag} + \frac{RT}{F}\ln\frac{K_{ap,\,AgCl}}{a_{Cl^-}} \qquad (22.11)$$

Let

$$a_{Cl^-} \approx a_{MeCl} = \gamma_{MeCl} m_{MeCl}$$

Our knowing $\gamma_{MeCl}$ allows us to calculate $K_{sp,\,AgCl}$. For cell (II) when MeCl = KCl experimental data give $E = -0.0456$ V at 298 K. Therefore the potential of the silver-silver chloride electrode (with KCl) relative to a hydrogen one is equal to 0.2882 V. From a table of the activity coefficients of salts for KCl at $m = 0.1$ and 25 °C we have $\gamma_{KCl} = 0.769$. Hence

$$0.2882 = 0.799 + 0.05916\log\frac{K_{sp,\,AgCl}}{0.769\times 0.1} \text{ and}$$

$$K_{sp,\,AgCl} = 1.75\times 10^{-10}$$

**22.8*. Complex Ion Formation. Dissociation Constants of Complex Ions.** Equation (20.15) for the electrode potential includes the activity (for dilute solutions—the concentration) of a free ion of a metal. Consequently, by measuring the e.m.f. of a concentration cell in one of whose solutions the metal ion is a constituent part of a complex ion which partly dissociates, namely,

$$[MX_n]^{(m-n)+} \longrightarrow M^{m+} + nX^-$$

we can determine the concentration of the free ion $M^{m+}$ in a solution of a complex salt and calculate the dissociation (unstability) constant for the ion $MX_n^{(m-n)+}$:

$$K_d = \frac{a_{M^{m+}}a^n_{X^-}}{a_{MX_n}}$$

The activity coefficients for the ions $M^{m+}$ and $X^-$ obtained upon the dissociation of stable complex ions (whose degree of dissociations is low) can be taken equal to unity.

In investigation of a complex salt it is first necessary to establish the composition of the complex ions $MX_n$. This can be done with the aid of potentiometric titration. Thus, in the potentiometric titration of a solution of $AgNO_3$ with a solution of KCN using a silver electrode we obtain the curve shown in Fig. 22.2. A sharp change of the electrode potential is observed twice. When one gramme-equivalent of $CN^-$ is introduced, complete precipitation of the ions $Ag^+$ from the solution takes place. With a further addition of $CN^-$ a sharp decrease takes place when two gramme-equivalents of $CN^-$ are introduced, i.e. at $n = 2$, and this gives the formula $Ag(CN)_2^-$ for the complex.

Systematic measurements make it possible to estimate the dissociation constant for a complex ion. Let us consider as an example the concentration cell

$$(-)\,\mathrm{Ag}\,|\,\overset{\mathrm{II}}{\underset{m_2}{\mathrm{KCN}}},\ \underset{m_1}{\mathrm{AgNO_3}}\,\|\,\overset{\mathrm{I}}{\underset{m_1}{\mathrm{AgNO_3}}}\,|\,\mathrm{Ag}\,(+) \qquad \text{(III)}$$

where $m_1$ and $m_2$ are the initial molalities of the salts, and $m_1 \ll m_2$.

In solution (II) the ion $Ag^+$ practically completely enters the complex ion $[Ag(CN)_2]^-$ whose dissociation

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^- \qquad \text{(a)}$$

determines the concentration of $Ag^+$ in solution (II) according to the equation for the e.m.f. of a concentration cell:

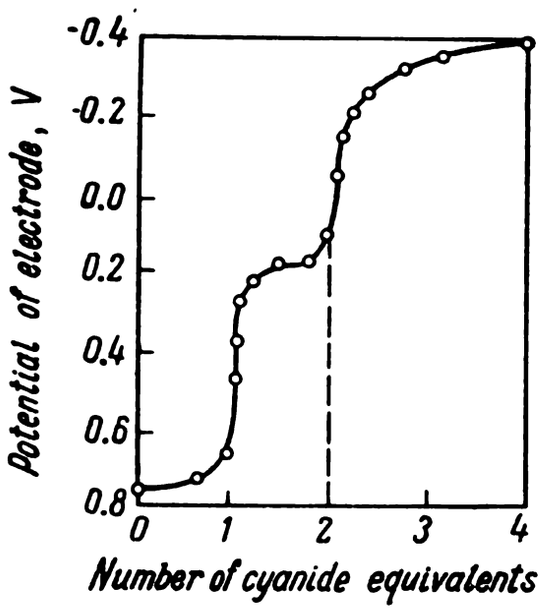



Fig. 22.2. Determining the composition of the complex $Ag(CN)_2^-$

$$E = \frac{RT}{F}\ln\frac{a^{\mathrm{I}}_{Ag^+}}{a^{\mathrm{II}}_{Ag^+}} \quad \text{and} \quad a^{\mathrm{I}}_{Ag^+} = m_1\gamma_{AgNO_3}$$

The dissociation constant for the ion $[Ag(CN)_2]^-$ in accordance with Eq. (a) is

$$K_d = \frac{a^{\mathrm{II}}_{Ag^+}a^2_{CN^-}}{a_{Ag(CN)_2^-}} \qquad (22.12)$$

and

$$a^{\mathrm{II}}_{Ag^+} = K_d\frac{a_{Ag(CN)_2^-}}{a^2_{CN^-}}$$

Assume that the activity coefficients of the ions are equal to the mean ionic activity coefficients. Almost all the silver in solution (II) enters into the composition of the complex, and for this reason $a_{Ag(CN)_2^-} = m_1\gamma_{KAg(CN)_2}$ and $a_{CN^-} = m_2\gamma_{KCN}$.

Let us insert the values of $a^{\mathrm{I}}_{Ag^+}$ and $a^{\mathrm{II}}_{Ag^+}$ into the equation for the e.m.f. of a concentration cell without transference

$$E = \frac{RT}{F}\ln\frac{m_1\gamma_{AgNO_3}m_2^2\gamma^2_{KCN}}{K_d m_1\gamma_{KAg(CN)_2}}$$

We consider that the mean ionic activity coefficients for the strong electrolytes $AgNO_3$ and $KAg(CN)_2$ are approximately identical and insert the value of $E = 1.3276$ V (experimental). The equation becomes

$$1.3276 = 0.05773\log\frac{m_2^2\gamma^2_{KCN}}{K_d}$$

According to tabulated data $\gamma_{KCN} \approx 0.5$ at $m_2 = 1$. For the dissociation constant of $Ag(CN)_2^-$ we get the value

$$K_d = 2.5 \times 10^{-24}$$

**22.9*. Ionic Product and Electrolytic Dissociation Constant of Water.** Let us prepare an electrochemical cell without transference

$$H_2 \mid \underset{m_1}{MeOH}, \underset{m_2}{MeX}, AgX(s) \mid Ag \qquad \text{(IV)}$$

where Me = $Li^+$, $Na^+$, $K^+$ or $Ba^{2+}$
X = $Cl^-$ or $Br^-$.

The solubility of AgX is less than that of AgOH by several orders. The following reaction proceeds in the cell:

$$\frac{1}{2} H_2 + AgX(s) = H^+ + X^- + Ag$$

and the e.m.f. is described by the equation

$$E_1 = E_1^\circ + \frac{RT}{F} \ln a_{HX} = E_1^\circ + \frac{RT}{F} \ln \gamma_{H^+}\gamma_{X^-} m_{H^+} m_{X^-} \qquad (22.13)$$

The electrolytic dissociation constant of water is determined by the equation

$$K_{d,\,H_2O} = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} = \frac{\gamma_{H^+}\gamma_{OH^-} m_{H^+} m_{OH^-}}{a_{H_2O}} \qquad (22.14)$$

Using the expression for $\gamma_{H^+} m_{H^+}$ from Eq. (22.14) in Eq. (22.13), we get

$$\frac{E_1 - E_1^\circ}{0.000\,195\,3T} = \log \frac{\gamma_{X^-} m_{X^-} K_{d,\,H_2O} a_{H_2O}}{\gamma_{OH^-} m_{OH^-}}$$

or

$$\frac{E_1 - E_1^\circ}{0.000\,195\,3T} + \log \frac{m_{OH^-}}{m_{X^-}} = \log \frac{\gamma_{X^-} a_{H_2O}}{\gamma_{OH^-}} + \log K_{d,\,H_2O} \qquad (22.15)$$

The concentrations of the ions are equal to those of the strong electrolytes MeOH and MeX:

$$m_{OH^-} = m_1 \quad \text{and} \quad m_{X^-} = m_2 \qquad (22.16)$$

By gradually reducing $m_1$ and $m_2$, we can find the limit which the left-hand part of Eq. (22.15) tends to when $(m_1 + m_2) \to 0$. In this case $\gamma_{OH^-} \to 1$ and $\gamma_{X^-} \to 1$, while the activity $a_{H_2O}$ in an infinitely dilute solution is also equal to the molality of water ($m_0 = 55.51$). Hence

$$\lim \left( \frac{E_1 - E_1^\circ}{0.000\,195\,3T} + \log \frac{m_1}{m_2} \right) = \log K_{d,\,H_2O} \times 55.51 =$$

$$= \lim \log K_w = \log m_{H^+} m_{OH^-} \qquad (22.17)$$

Here $K_w$ is the product of the activities of water $a_{H^+} a_{OH^-}$.

Below are given the values of $K_w \times 10^{14}$ at different temperatures obtained from e.m.f. measurements in cells IV with Me = $K^+$, $Na^+$, $Ba^{2+}$ or $Li^+$ and X = = $Cl^-$ or $Br^-$ with discrepancies of 1-1.5% in the values of $K_w$ calculated from data for separate combinations of ions.

| $t$, °C | 0 | 10 | 20 | 25 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|---|---|---|
| $K_w \times 10^{14}$ | 0.1136 | 0.2920 | 0.6809 | 1.008 | 1.469 | 2.919 | 5.474 | 9.614 |

To be able to determine the ionic product of water $m_{H^+}m_{OH^-}$ from Eq. (22.14) according to the value of $K_w$, it is necessary to know $\gamma_{H^+}\gamma_{OH^-}/a_{H_2O}$, the "activity function" of the ions of water. For this purpose, in addition to the values of $E_1 - E_1^\circ$, it is necessary to measure the e.m.f.s of the cells

$$\underset{}{\mathrm{Pt,\ H_2\,|\,}}\underset{m_3}{\mathrm{HX}},\ \underset{m_2}{\mathrm{MeX}}\ \|\ \underset{m_2}{\mathrm{MeX}},\ \mathrm{AgX(s)\,|\,Ag} \qquad \text{(V)}$$

and, by forming cells without transference from them, compute the e.m.f.s of cells of the following kind:

$$\mathrm{Pt,\ H_2\,|\,}\underset{m_3'}{\mathrm{HX}},\ \underset{m_2'}{\mathrm{MeX}}\ \|\ \underset{m_3}{\mathrm{HX}},\ \underset{m_2}{\mathrm{MeX}}\,|\,\mathrm{H_2,\ Pt} \qquad \text{(VI)}$$

In Sec. 22.1 we considered a method of calculating the activity coefficients $\gamma_{(HX)}$ for solutions with any concentrations of MeX and HX from the values of the e.m.f.s for cells of kind (VI). Now we can insert $\gamma_{X^-} = \gamma_{HX}/\gamma_{H^+}$ into Eq. (22.15), use conditions (22.16) and transform expression (22.15):

$$\frac{E_1 - E_1^\circ}{0.000\,195\,3T} + \log\frac{m_1}{m_2} - \log K_{d,\,H_2O} = \log\frac{\gamma_{HX}a_{H_2O}}{\gamma_{H^+}\gamma_{HO^-}} \qquad (22.18)$$

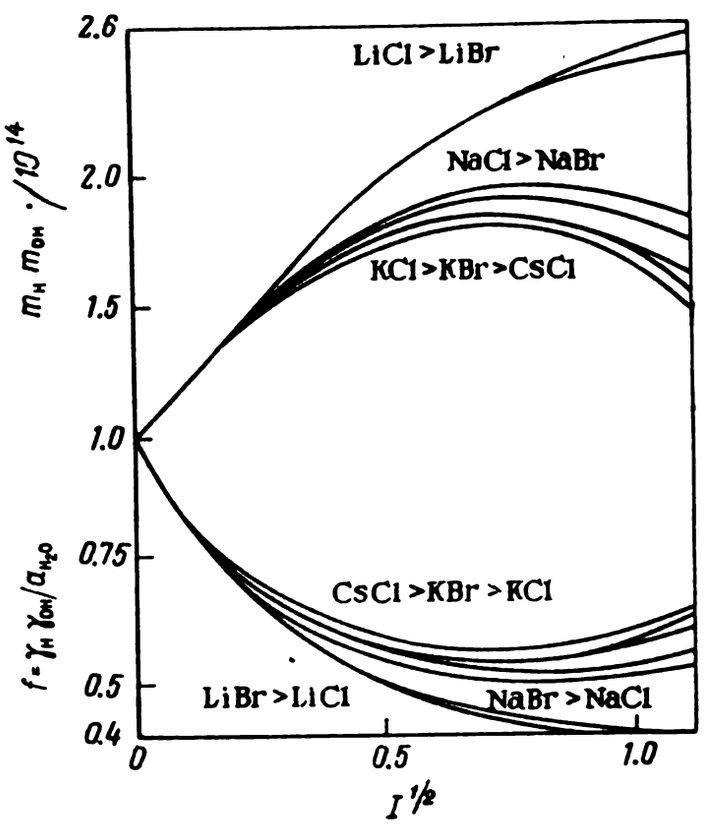



Fig. 22.3. Activity function of ions $f$ and ionic product of water $m_{H^+}m_{OH^-}$ in solutions of salts versus square root of ionic strength

We can now find the value of $\gamma_{H^+}\gamma_{OH^-}/a_{H_2O} = f$ (the activity function of water ions) for any investigated combinations of the concentrations $m_1$ and $m_2$ by means of Eq. (22.17) and, therefore, use Eq. (22.14) to calculate $m_{H^+}m_{OH^-}$, the ionic product of water. Figure 22.3 shows the function $f$ and the ionic product $m_{H^+}m_{OH^-}$ of water versus $I^{1/2}$ for solutions of various salts. The activity of undissociated molecules of water as a non-electrolyte comparatively sparsely depends on the ionic strength of a solution. The dependence of $\gamma_+\gamma_- = \gamma_\pm^2$ on $I$ is the basic one. In accordance with the electrostatic theory, the square of the mean ionic activity coefficient $\gamma_\pm^2$ is equal to unity when $I = 0$, diminishes with a growth of $I$, and then passes through a minimum. The ionic product of water correspondingly passes through a maximum. For an infinitely dilute solution $m_{H^+}m_{OH^-} = 1.008 \times 10^{-14}$ at 25 °C and grows 1.5-2 times when $I^{1/2} = 0.5$-$0.8$, i.e. $I = 0.2$-$0.6$.

**22.10. Calculation of Gibbs Energy of Solvation of Ions in a Solution.** In Sec. 20.5 we mentioned the problem of determining the activity coefficients for separate ions and the dissociation constants with account of these coefficients. At present methods for determining these quantities are only beginning to be developed. N. Izmailov was the first to calculate the change in the Gibbs energy of ions of one species in hydration and in solvation in a number of non-aqueous solvents. He based his calculations on the e.m.f.s of cells with or without transference and considered the work of a cell as the result of the change in the Gibbs energy upon the transfer of the substance of each electrode into the solution with the formation of a solvated ion. The possibility of such a calculation was established somewhat earlier by V. Pleskov.

Let us consider a cell prepared of two metals, $Me_1$ and $Me_2$, and solutions of the corresponding ions

$$Me_1 \mid Me_1^+ \mid Me_2^+ \mid Me_2 \mid Me_1$$

If we neglect the diffusion potential, the e.m.f. of the cell is determined by the equation

$$E = -\frac{(\Delta G_{B,1} - \Delta G_{B,2}) + (\Delta G_{A,1} - \Delta G_{A,2}) + (\Delta G_{C,1} - \Delta G_{C,2})}{zF} \qquad (22.19)$$

where $\Delta G_{B,1}$ and $\Delta G_{B,2}$ = changes in the Gibbs energy of the metals $Me_1$ and $Me_2$ upon their sublimation

$\Delta G_{A,1}$ and $\Delta G_{A,2}$ = ditto upon their ionization in a vacuum

$\Delta G_{C,1}$ and $\Delta G_{C,2}$ = ditto upon solvation of the ions formed.

If one electrode is a hydrogen one, then instead of the corresponding energy of sublimation it is necessary to take $\frac{1}{2}D$ (where $D$ is the energy of dissociation of a gramme-molecule of hydrogen).

It is quite obvious that the calculation of the quantities $\Delta G_{C,1}$ and $\Delta G_{C,2}$ for the solvation of ions is the most difficult in the calculations of the activity coefficients of ions.

Let us consider the following cell without transference

$$(-)Ag \mid HCl, aq; \quad AgCl(s) \mid HCl, aq \mid Pt, H_2(+)$$

On the basis of Eq. (22.19) we write [$z = 1$; the subscript 1 in Eq. (22.19) is Ag, $Ag^+$, and 2 is H, $H^+$]:

$$\Delta G_{C,H^+} - \Delta G_{C,Ag^+} = EF - \left(\frac{1}{2}D_{H_2} + \Delta G_{A,H}\right) + \Delta G_{B,Ag} + \Delta G_{A,Ag} \qquad (22.20)$$

Since AgCl forms a saturated solution (the crystals of AgCl and the solvated ions $Ag^+$ and $Cl^-$ are in equilibrium), the value of $\Delta G$ for the solution of AgCl is equal to zero

$$\Delta G = 0 = U_{0,AgCl} + \Delta G_{C,Ag^+} + \Delta G_{C,Cl^-} \quad \text{and} \quad \Delta G_{C,Ag^+} + \Delta G_{C,Cl^-} = -U_{0,AgCl}$$

where $U_0$ is the electrostatic energy of decomposition of the crystal lattice into unsolvated ions (an ideal gas) related to 0 K and equal to the change in $G$ in this process (see Vol. 1, Sec. 2.3). Inserting $\Delta G_{C,Ag^+}$ from the last expression into Eq. (22.20), we get

$$\Delta G_{C,H^+} + \Delta G_{C,Cl^-} = EF - \left(\frac{1}{2}D_{H_2} + \Delta G_{A,H}\right) + (\Delta G_{B,Ag} + \Delta G_{A,Ag}) - U_{0,AgCl} \qquad (22.20a)$$

All the quantities in the right-hand part of Eq. (22.20) can be measured. It is thus possible to find the sum for the energies of solvation of both ions. If we

take a cell with transference, then the left-hand part of a similar equation will include not the sum, but the difference between the corresponding values of $\Delta G_C$ of solvation.

Using such data for the values of $\Delta G$ of dissociation, sublimation, ionization, the energy of a crystal lattice and the values of $E$ for a cell having a different solvent (not water), we can find the sum or difference of the values of $\Delta G_C$ of solvation of ions in non-aqueous solvents.

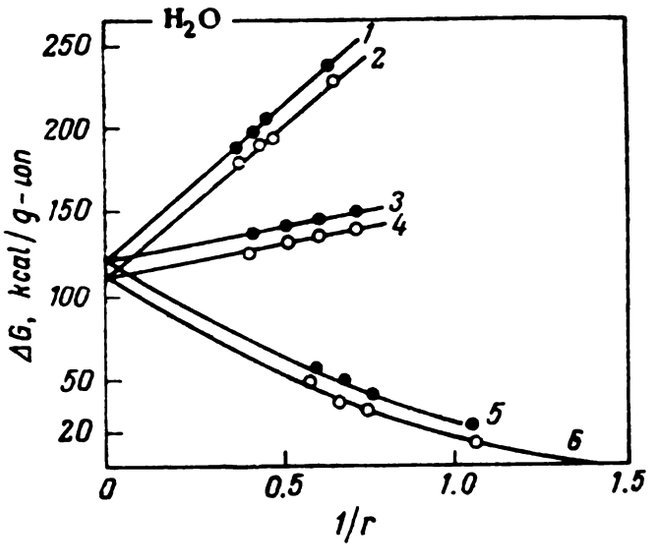



Fig. 22.4. Dependence on $1/r$ in water of quantities:

1 – $\Delta G_{C,Li}+\Delta G_{C,Hal}$; 2 – $\Delta G_{C,Ag}+\Delta G_{C,Hal}$;

3 – $\Delta G_{C,Li}+\frac{\Delta G_{C,Hal}-\Delta G_{C,Me}}{2}$;

4 – $\Delta G_{C,Ag}+\frac{\Delta G_{C,Hal}-\Delta G_{C,Me}}{2}$;

5 – $\Delta G_{C,Ag}-\Delta G_{C,Me}$; 6 – $\Delta G_{C,Li}-\Delta G_{C,Me}$;

$r$ – radius of halide (Hal) or metal (Me) ion. The extrapolated values are $\Delta G_{C,Li}=117.0$ and $\Delta G_{C,Ag}=112.0$

To terminate the calculation, i.e. compute the values of the quantities, it is necessary to divide the sums or differences obtained by the separate addends for different ions. This cannot be done by the method of e.m.f.s. A different way must be found. N. Izmailov proposes a method that is identically applicable to all solvents regardless of their properties. This method consists in the following. The sums (or correspondingly the differences) of $\Delta G_C$ are calculated for a number of substances that are a combination of the same ion with a number of different ions whose radii $r$ gradually grow (for example, the series of hydrogen, lithium or silver halides). Next the values of the found sums $\Delta G_C$ are plotted on a chart along the axis of ordinates, and the values of $1/r$ (where $r$ are the corresponding radii of the ions of the series being investigated, in the given case halide ions) along the axis of abscissae. The points plotted in this way lie on a curve (close to a straight line) that can be extrapolated to $1/r = 0$, i.e. to $r = \infty$. With a growth of $r$ the value of $\Delta G_{C,Hal}$ tends to zero. For this reason in the limit $\Delta G_{C,H} + \Delta G_{C,Hal} = \Delta G_{C,H}$ (correspondingly $\Delta G_{C,Li}$) is the length cut off on the axis of ordinates by the extrapolated curve.

If we consider a series of cells with transference prepared, for example, from a hydrogen half-cell and half-cells formed from amalgams of alkali metals and the solutions of the relevant salts, then the values of the obtained differences $\Delta G_{C,H} - \Delta G_{C,Me}$ plotted against $1/r$ (where $r$ denotes the radii of the ions of the alkali metals) also give a series of points lying on a curve close to a straight line. Such series of values can be obtained by replacing the hydrogen ion (and, corresponding y, the half-cell), for example, with $Li^+$ or $Ag^+$. The charts in Figs. 22.4 and 22.5 (for aqueous and ammonia solutions) show that both for cells with $Li^+$ and for ones with $Ag^+$ in both series (with Hal and with Me ions) the continuations of the curves cut off practically the same length on the axis of ordinates[1]. After finding the values of $\Delta G_{C,Li}$ or $\Delta G_{C,Ag}$ by means of

[1] Figures 22.4 and 22.5 also contain auxiliary curves *3* and *4*. It was found that the sum, for example

$$\Delta G_{C,Li+}+\frac{\Delta G_{C,Hal}-\Delta G_{C,Me}}{2}=f\left(\frac{1}{r_m}\right)$$

extrapolation, we can use the sums and differences to determine the values of $\Delta G_C$ for other ions, in the same way as in calculating the absolute mobilities from

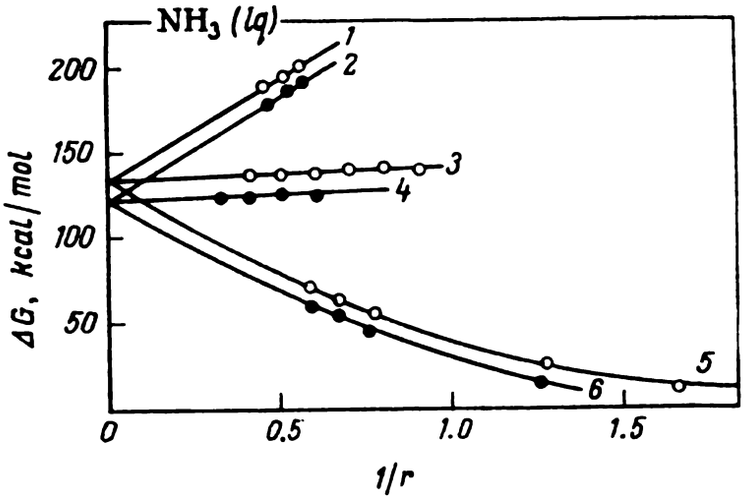



Fig. 22.5. Dependence of $1/r$ in liquid ammonia on quantities: 1 – $\Delta G_{C,Ag}+\Delta G_{C,Hal}$; 2 – $\Delta G_{C,Li}+\Delta G_{C,Hal}$; 3 – $\Delta G_{C,Ag}+\frac{\Delta G_{C,Hal}-\Delta G_{C,Me}}{2}$; 4 – $\Delta G_{C,Li}+\frac{\Delta G_{C,Hal}-\Delta G_{C,Me}}{2}$; 5 – $\Delta G_{C,Ag}-\Delta G_{C,Me}$; 6 – $\Delta G_{C,Li}-\Delta G_{C,Me}$; $r$ – radius of halide (Hal) or metal (Me) ion. The extrapolated values are $\Delta G_{C,Li}=124.0$ and $\Delta G_{C,Ag}=132.0$

the values of the equivalent conductivities $\Lambda_\infty$. Such calculations have resulted in the values of the Gibbs energies of solvation of ions in aqueous, ammonia and other solutions given in Table 22.1.

TABLE 22.1

**Gibbs Energies of Solvation $\Delta G_C$ of Ions in Selected Solvents (according to Izmailov)**

| Ion | $\Delta G_C$ in solvent, kcal/g-ion | | | |
|---|---|---|---|---|
| | $NH_3$ | $H_2O$ | $C_2H_5OH$ | HCOOH |
| $H^+$ | 281.0 | 258.0 | 252.0 | 246.0 |
| $Li^+$ | 124.0 | 117.0 | 115.0 | 116.0 |
| $Na^+$ | 99.0 | 96.0 | 90.0 | 99.5 |
| $K^+$ | 79.4 | 78.0 | | |
| $Rb^+$ | 74.3 | 74.4 | 73.0 | 73.0 |
| $Cs^+$ | 65.6 | 64.0 | — | 65.0 |
| $Ag^+$ | 132.0 | 112.0 | 108.0 | 120.8 |
| $Ca^{2+}$ | 360.0 | 372.4 | — | 209.2 |
| $Zn^{2+}$ | 563.0 | 492.0 | 473.5 | 488.3 |
| $Cd^{2+}$ | 546.0 | 430.0 | 413.0 | 410.4 |
| $Cl^-$ | 65.5 | 74.0 | 71.3 | 78.3 |
| $Br^-$ | 62.8 | 68.0 | 66.2 | — |
| $I^-$ | 57.0 | 59.4 | 58.5 | — |

is a linear function of the mean value of the reciprocal radii $\frac{1}{r_m}=\frac{1}{2}\left(\frac{1}{r_{Hal}}+\frac{1}{r_{Me}}\right)$. Plots show that these straight lines have a small inclination for aqueous solutions and are almost horizontal for ammonia ones (in the latter instance the half-difference $\Delta G = 0$). These lines are easily extrapolated to $1/r_m = 0$ and give the same lengths on the axis of ordinates as the main curves.

# CHAPTER 23

# CHEMICAL SOURCES OF ELECTRIC CURRENT

**23.1. Accumulators.** In principle any electrochemical cell can serve as a source of an electric current. When the extreme electrodes are connected by a metal conductor, the presence of an e.m.f. will cause electrons to migrate along the conductor from the electrode with the greater negative potential to the one with the smaller negative potential. Simultaneously electrochemical reactions proceed on the surface of the electrodes whose energy serves as a source of the electrical energy liberated into the external circuit. For various reasons (a low electrical capacity, a low rate and irreversible nature of the chemical reactions, physical changes in the electrodes in service, etc.), the majority of cells cannot be used practically for obtaining an electric current, and only a few of them have found application as *chemical sources of current.*

Chemical sources of current are divided into sources with *one-time action* (*galvanic cells*) and *with repeated action* (*storage cells or accumulators*).

When an electric current from an external source is passed through an accumulator (charging) chemical changes occur at the electrodes and in solutions that are close to reversible ones, and the work of the electric current is accumulated (stored) in the form of free energy of the reaction products. A charged accumulator produces an electric current during its discharging, after which it can be charged again.

The most widely used accumulators are the lead-acid, cadmium-nickel alkaline and silver-zinc alkaline ones.

A *lead accumulator* in the charged state is the cell

$$(-)\,Pb,\ PbSO_4\,(s)\,|\,H_2SO_4\,(32\text{-}34\%)\,|\,PbO_2,\ Pb(+)$$

The following electrode reactions proceed during its operation: at the left electrode

$$Pb + SO_4^{2-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} PbSO_4(s) + 2e \qquad \text{(I)}$$

at the right electrode

$$PbO_2(s) + 4H^+ + SO_4^{2-} + 2e \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} PbSO_4(s) + 2H_2O \qquad \text{(II)}$$

total reaction

$$Pb + PbO_2(s) + 4H^+ + 2SO_4^{2-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} 2PbSO_4(s) + 2H_2O \qquad (III = I + II)$$

The Gibbs energy $\Delta G$ of this reaction corresponds to the disappearance of the solid Pb and $PbO_2$, the appearance of the solid $PbSO_4$, and also the disappearance of two moles of $H_2SO_4$ and the appearance of two moles of $H_2O$:

$$\Delta G = 2\mu_{PbSO_4} + 2\mu_{H_2O} - \mu_{Pb} - \mu_{PbO_2} - 2\mu_{H_2SO_4}$$

Since the chemical potentials of the solid phases are constant (at the given temperature and pressure), we have

$$2\mu_{PbSO_4} - \mu_{Pb} - \mu_{PbO_2} = \text{const} = C$$

$$\Delta G = C + 2\mu^\circ_{H_2O} + 2RT \ln a_{H_2O} - 2\mu^\circ_{H_2SO_4} - 2RT \ln a_{H_2SO_4}$$

$$E = -\frac{\Delta G}{2F} = \frac{-C - 2\mu^\circ_{H_2O} + 2\mu^\circ_{H_2SO_4}}{2F} + \frac{RT}{2F} \ln \frac{a^2_{H_2SO_4}}{a^2_{H_2O}} =$$

$$= E^\circ + \frac{RT}{F} \ln \frac{a_{H_2SO_4}}{a_{H_2O}} = E^\circ + \frac{RT}{F} \ln \frac{\gamma^3_\pm \times 4m^3}{a_{H_2O}} \qquad (23.1)$$

The value of $a_{H_2SO_4}$ in the above equation has been found in accordance with the relations set out in Sec. 16.4, namely,

$$a_{H_2SO_4} = a^3_\pm = \gamma^3_\pm m^3_\pm = \gamma^3_\pm (\nu^\nu_+ \nu^\nu_-) m^3 = \gamma^3_\pm (2^2 \times 1^1) m^3 = \gamma^3_\pm \times 4m^3$$

The quantities $\Delta G$ and $E$ for an accumulator depend on the concentration of the sulphuric acid (more exactly, on the activity of the solution components).

Direct experiments result in obtaining the value of $E^\circ$ for a lead accumulator [Eq. (23.1)]. For a 27.3% solution of $H_2SO_4$ ($m = 3.83$) the value of $\gamma_\pm = 0.165$. The activity of water is easily computed from the pressures of the saturated vapour of water over the solution and over pure water according to the equation $a_{H_2O} = p/p^\circ$ and is equal to 0.7 for the solution considered above. The e.m.f. of an accumulator containing an acid of the concentration given above is equal to 2.007 V. Using these data in Eq. (23.1), we get

$$E^\circ = 2.007 - 0.059\,16 \log \frac{0.165^3 \times 4 \times 3.83^3}{0.7} = 1.997 \text{ V}$$

Knowing the values of $\gamma_\pm$ and $p_{H_2O}$ for solutions of sulphuric acid of different concentrations, we can use Eq. (23.1) to compute the e.m.f. of a lead accumulator filled with $H_2SO_4$ of a definite concentration.

The e.m.f. of a lead accumulator can be calculated by means of tables of standard potentials (20.1 and 20.2). Accurate calculation, however, is difficult owing to the fact that the solubilities of $PbO_2$ and $PbSO_4$ are very low.

At the negative electrode $Pb^{2+} \mid Pb$ we have $\varphi^\circ_{Pb} = -0.126$ V

$$\varphi_{Pb} = \varphi^\circ_{Pb} + \frac{RT}{2F} \ln a_{Pb^{2+}}$$

We find the activity of a lead ion from the activity product for a saturated solution of $PbSO_4$, which at 25 °C is equal to

$$K_{ap} = a_{Pb^{2+}} a_{SO_4^{2-}} = 2.2 \times 10^{-8}$$

$$a_{Pb^{2+}} = \frac{K_{ap}}{a_{SO_4^{2-}}}$$

$$\varphi = \varphi^\circ_{Pb} + \frac{RT}{2F} \ln \frac{K_{ap}}{a_{SO_4^{2-}}} = \varphi^\circ_{Pb} + \frac{RT}{2F} \ln K_{ap} - \frac{RT}{2F} \ln a_{SO_4^{2-}} =$$

$$= -0.126 - 0.226 - \frac{0.059\,16}{2} \log a_{SO_4^{2-}}$$

The concentration and activity of $Pb^{4+}$ in solutions of sulphuric acid saturated with $PbO_2$ and also the standard potential of the electrode $Pb^{4+} \mid Pb$ ($\varphi^\circ \approx 0.7$ V) are known with insufficient accuracy. In Table 20.2 we can find the standard potential of the positive accumulator electrode

$$PbSO_4,\ PbO_2,\ H_2SO_4 \mid Pb\ ;\ \varphi^\circ_{PbO_2,\ PbSO_4} = 1.685\ V$$

In accordance with the equation of the reaction on the positive electrode of the accumulator [reaction (II)] its potential is expressed by the equation

$$\varphi_{PbO_2,\ PbSO_4} = \varphi^\circ_{PbO_2,\ PbSO_4} - \frac{RT}{2F} \ln \frac{a^2_{H_2O}}{a^4_{H^+} a_{SO_4^{2-}}} =$$

$$= 1.685 - \frac{0.059\,16}{2} \log \frac{a^2_{H_2O}}{a^4_{H^+} a_{SO_4^{2-}}}$$

Summation of the electrode potentials gives the e.m.f. of a lead accumulator

$$E = \varphi_{PbO_2,\ PbSO_4} - \varphi_{Pb^{2+}} = 1.685 + 0.352 +$$

$$+ \frac{0.059\,16}{2} \log \frac{a^4_{H^+} a_{SO_4^{2-}}}{a^2_{H_2O}} + \frac{0.059\,16}{2} \log a_{SO_4^{2-}}$$

whence

$$E = 2.037 + 0.059\,16 \log \frac{a^2_{H^+} a_{SO_4^{2-}}}{a_{H_2O}} \qquad (23.2)$$

Since (see Sec. 16.4)

$$a^2_{H^+} a_{SO_4^{2-}} = a^3_{\pm} = \gamma^3_{\pm} 4m^3$$

Eq. (23.2) is transformed into the equation

$$E = 2.037 + 0.059\,16 \log \frac{\gamma^3_{\pm} 4m^3}{a_{H_2O}} \qquad (23.3)$$

which agrees quite well with Eq. (23.1).

In the discharge of an accumulator, the concentration of the sulphuric acid decreases, and in charging the solution again becomes more concentrated.

An *alkaline nickel-cadmium accumulator* in the charged state is the following electrochemical cell

$$(-)Cd|\ Cd(OH)_2,\ KOH(20\%)\ ||\ KOH(20\%),\ Ni(OH)_2,\ Ni(OH)_3\ |\ Ni(+)$$

The total reaction in this cell is

$$Cd + 2Ni(OH)_3 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Cd(OH)_2 + 2Ni(OH)_2$$

The value of $\Delta G$ for this reaction should not depend on the concentration of the alkali, since only solids participate in the total reaction. The reactions on the electrodes, however, are accompanied by a change in the concentration of the alkali and the formation of a difference between the concentrations at the two electrodes

$$Cd + 2OH^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Cd(OH)_2 + 2e$$

$$2Ni(OH)_3 + 2e \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2Ni(OH)_2 + 2OH^-$$

This difference should result in concentration polarization that reduces the e.m.f. of the cell. As a result of natural mixing in conditions of closeness of the electrodes, however, this difference of concentrations does not practically appear.

The e.m.f. of a nickel-cadmium accumulator is about 1.36 V. Alkaline accumulators are also used in which the cadmium and cadmium oxide are replaced by iron and ferrous oxide.

In a *zinc-silver accumulator* a porous zinc plate is the anode and the silver oxides $Ag_2O$ and AgO obtained by the electrolytic oxidation of metal silver are the cathode. The electrolyte is a concentrated solution of KOH saturated with potassium zincate $Zn(OK)_2$. The charged accumulator can be symbolized as

$$(-)Zn\ |\ Zn(OK)_2 + KOH\ (40\%)\ |\ AgO \text{ or } Ag_2O\ |\ Ag(+)$$

The total reaction in this cell is

$$AgO + Zn \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} ZnO + Ag$$

The process proceeds in two steps. First the AgO is reduced to $Ag_2O$ and then to metallic silver. The e.m.f. of cells with the cathode AgO is equal to 1.86 V, and with the cathode $Ag_2O$ to 1.58-1.60 V (at 25 °C). At low current densities the voltage drops by 0.3 V when passing over from the first step to the second one. Practically only the second step is used.

After discharge of the accumulator we have

$$(-)Zn \mid ZnO,\ Zn(OK)_2 + KOH(40\%) \mid Ag(+)$$

In these accumulators, in contrast to the lead and alkaline ones, the electrolyte does not participate in the charge and discharge reactions. For this reason a very small amount of it may be taken. This circumstance made it possible to create accumulators having a very effective design, namely, the electrodes are placed close to each other and are separated by only a thin layer of cellophane. The entire electrolyte is in the pores of the electrodes. Zinc-silver accumulators have a high capacity, a high energy and a high power per unit of mass and volume. This is why they are widely used where accumulators of a small size are required.

**23.2. The Problem of Fuel Cells.** The operation of any chemical source of current is accompanied by a total chemical reaction between an oxidizer (the active substance of the positive electrode) and a reducer (the active substance of the negative electrode). The maximum electrical work obtained in the operation of a source of current is equal to the decrease in the Gibbs energy for this reaction:

$$W' = -\Delta G$$

The chemical energy of a reaction of interaction of an oxidizer (the oxygen of the air) and a reducer (fuel) is also used for the industrial production of electrical energy at heat power plants. In this case, however, the conversion of energy follows a complicated path. The chemical energy is first transformed into heat, then into mechanical energy and only then into electrical energy. The maximum electrical work obtained in such a conversion is determined by the heat of the reaction ($Q_p = \Delta H$):

$$W' = Q_p \frac{T_1 - T_2}{T_1}$$

Theoretically the effectiveness of transforming chemical energy into electrical energy through heat is very low. For this reason already at the end of the 19th century scientists attempted to create devices for the direct conversion of chemical into electrical energy.

This requires the development of galvanic cells in which the reactions of oxidation of the fuel and reduction of oxygen proceed electrochemically. The first attempts to create such *fuel cells* were not successful owing to the very low rate of the reaction of electrochemical oxidation of the usual kinds of fuel. Only in the last few years as a result of employing various catalysts and improving the design of the cells did scientists succeed in creating the first satisfactorily functioning laboratory models of fuel cells using gaseous fuel. The most reactive kind of fuel is hydrogen. Hydrogen-oxygen

cells are generally made with the use of finely porous carbon or nickel electrodes immersed in an alkaline solution of an electrolyte. Such a cell can be symbolized as follows:

$$(-)(Ni)\,H_2 \mid KOH\ (30\text{-}40\%) \mid O_2(Ni)(+)$$

During operation of the cell, the following electrode reactions proceed:
at the negative electrode

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

at the positive electrode

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

The summary reaction is

$$2H_2 + O_2 \rightarrow 2H_2O(lq)$$

It was indicated in Sec. 20.11 that the theoretical value of the e.m.f. of a hydrogen-oxygen cell at 25 °C is equal to 1.229 V and that it does not depend on the composition of the electrolyte solution.

During the discharge of a hydrogen-oxygen cell the voltage is within 0.7-0.9 V depending on the density of the discharge current on the electrodes (in the best designs of cells the current density reaches 200-300 mA/cm$^2$).

Other kinds of gaseous fuel (carbon monoxide, hydrocarbons) can practically be used in fuel cells only at elevated temperatures (above 400-500 °C). The electrolyte used in such high-temperature cells is either a melt of an alkali metal carbonate or a solid electrolyte with anionic (oxygen) conductance.

Attempts to directly use solid coal in fuel cells have not been successful to date. Coal can be used only after its preliminary gasification. If the latter is performed with the aid of $CO_2$, the following sequence of reactions is observed:
gasification

$$C + CO_2 \rightarrow 2CO$$

in the fuel cell

$$2CO + O_2 \rightarrow 2CO_2$$

the total reaction

$$C + O_2 \rightarrow CO_2$$

At present the development of fuel cells is still in its initial stage. In principle the possibility of using certain kinds of fuel in such cells and the conversion of its chemical energy into electrical energy

with a practical efficiency up to 75-90% (in heat engines the efficiency does not exceed 40%) has been proved. Owing to various technological and operational difficulties (the insufficient period of service, increased requirements to the purity of the fuel, etc.), however, the economical advantages of fuel cells even with their higher efficiency of using the fuel are still not clear. For this reason the possibility of using them for the production of electrical energy instead of heat power plants requires further studying. There is no doubt, however, that for more limited purposes fuel cells will find broad application in the nearest future.

# CHAPTER 24

# KINETICS OF ELECTROCHEMICAL PROCESSES

**24.1. General. Electrolysis.** In the previous chapters we considered the equilibrium states of processes in electrolytes with the participation of ions (electrolytic dissociation, hydrolysis, solvation, etc.) and of processes at electrodes (electrochemical reactions and the parameters characterizing them—reversible electrode potentials). These states do not depend on time, and the two fundamental laws of thermodynamics can be applied to them. The corresponding laws that govern the equilibrium states of these processes are therefore called thermodynamic ones, and the branch of electrochemistry devoted to them—the *thermodynamics of electrochemical processes.* For electrode processes equilibrium is characterized by the absence of an electric current.

The process of the flow of an electric current of a finite intensity is not an equilibrium one, and the phenomena connected with the flow of a current depend on time. We have already considered such phenomena as the electrical conductance of electrolytes, and have touched upon friction phenomena. These phenomena are accompanied by a change in the state of a solution and its separate parts with time[1]. In addition, the parameters characterizing a process depend on the current intensity, whose magnitude can be regulated externally.

In this chapter we deal with electrode processes in their dependence on the current intensity, i.e. non-equilibrium, mainly stationary processes proceeding on electrodes with time. This branch of electrochemistry is called the *kinetics of electrochemical* (or *electrode*) *processes* or briefly *electrochemical kinetics*[2].

Electrochemical kinetics is based on the general laws of chemical kinetics and on particular laws characteristic only of electrochemical

[1] In observance of the constancy of known boundary conditions, the state of each part of a solution may remain unchanged during an indefinitely long interval of time when a current flows through it. Non-equilibrium states of this kind are called *stationary* ones. Such states are also possible in the transfer of heat, the diffusion of a solute and in other irreversible processes.

[2] The theory of the electrical conductance of solutions is usually not included in this branch, although formally it is a part of electrochemical kinetics, if the theory of electrolytes is considered to be a part of electrochemistry, and not of the theory of solutions.

processes. Thus, it is necessary to note the applicability to electrochemistry of the basic postulate of chemical kinetics, of the concept of activation energy to many electrochemical processes, the positive influence of temperature on the rate of electrolysis, etc.

An electric current can flow as a result of connecting the circuit of an electrochemical cell formed by electrodes and an electrolyte, or of applying an external potential difference to the system electrodes-electrolyte. In the latter case the phenomena occurring at the electrode-electrolyte interfaces are called *electrolysis* and consist in the liberation of substances (metals, gases) from the electrolyte at the electrode, in dissolving of the substance of an electrode and in a change in the composition of the electrolyte at an electrode.

Electrolytic methods of producing metals (aluminium, magnesium) from salt melts, gaseous chlorine and a solution of alkali from sodium chloride solutions, persulphate, perchlorate and permanganate, the oxidation and reduction of organic substances (the production of iodoform, the electrolytic chlorination of benzene, the electrolytic reduction of nitrobenzene) and many other technical applications of electrolysis are acquiring greater and greater significance.

The specific nature of electrochemical processes is expressed quite clearly, together with their obeying the general laws of the kinetics of heterogeneous processes.

It must be noted first of all that some reactions which do not proceed chemically at ordinary temperatures can proceed electrochemically. Spontaneous reactions are always accompanied by a decrease in the free energy. Electrochemical means allow us to conduct reactions accompanied by an increase in the free energy. For example, the reaction of decomposition of water does not proceed at ordinary temperatures, but the process of combination of hydrogen with oxygen in the presence of a catalyst proceeds quite easily. By electrochemical means (electrolysis) water is easily decomposed even at ordinary temperatures.

The possibilities of electrosynthesis are broader than those of ordinary chemical synthesis, since the required free energy is supplied to the system from outside in the form of the energy of an electric current.

The total rate of an electrochemical process can not only be easily determined from the intensity of the current flowing through a cell, but can also be controlled by changing the current intensity.

The rate of an electrochemical process depends on the e.m.f., i.e. on the difference of potentials between the electrodes, and appreciably depends on the conditions of diffusion of the ions. Similarly, the rate of a separate electrode process depends on the potential of the electrode. The diffusion of the ions frequently has a determining influence on the rate of an electrode process.

The activation energy of an electrochemical process is often related to the potential drop in the electrical double layer. In other words, the presence of an electrostatic field at the electrode-solution interface should affect the rate of an electrochemical process, since the latter is related in some way to the migration of the charged particles through this interface.

As previously indicated, an electric current causes changes on the surface of electrodes that depend on many factors and first of all on the current intensity. The change in the electrical state of an electrode (its potential, density of charge of the electrical double layer) under the influence of the electric current passing through the interface is called *polarization of the electrode.* Let us treat consecutively with concentration polarization and chemical or electrochemical polarization of electrodes. In polarization, the potential of an electrode changes in comparison with the "equilibrium" value that it had in the given solution in the absence of current. In changing it may either remain an equilibrium one corresponding to electrochemical equilibrium between the electrode and the solution in the new conditions, or become a non-equilibrium one. In the latter case an overpotential (overvoltage) is present.

**24.2. Exchange Currents.** Equilibrium between a solution and an electrode having a definite potential is dynamic equilibrium in which a continuous exchange of charged particles between the electrode and the solution takes place. In equilibrium the rates of transition of these particles in opposite directions are identical. The quantity of electricity passing in these conditions in a unit of time from the electrode into the solution and vice versa is called the *exchange current.*

The existence of an exchange current can be proved by the method of isotope indicators. Thus, if we immerse a plate of platinized platinum saturated with hydrogen into a solution containing heavy water, we can trace deuterium in the gaseous phase after a certain time has elapsed. Its amount allows us to calculate the intensity of the exchange current[1].

Ideally polarizable electrodes, in which the surfaces of the electrical double layer may be in electrostatic equilibrium and not

[1] It must be indicated, however, that the exchange current found in this way is not equal to the exchange current of the system $H_3O^+ \mid H_2$, Pt, since there is a certain difference between the reactivity of the different hydrogen isotopes. The exchange current between gaseous deuterium and deuterium ions is somewhat less than that between gaseous hydrogen and hydrogen ions. The electrolytic separation of hydrogen and deuterium is based on the difference in their exchange currents (and, apparently, in overvoltages). In the electrolysis of a mixture consisting of ordinary and heavy water, the hydrogen is liberated easier than the deuterium. The latter concentrates in the solution in the form of heavy water.

exchange charged particles in the absence of a current, behave differently.

It is obvious that when an electric current passes through an electrode-solution interface, a two-directional exchange current is present, but as a rule an incomparably greater unidirectional current is superposed onto it. The latter is determined by the e.m.f. of the cell or the applied external potential difference. The magnitude of the exchange current, which is reverse in direction to the current applied from an external source, may change in comparison with equilibrium conditions (the absence of a current), since it depends on the potential of the electrode, the concentration polarization and other factors.

**24.3. Concentration Polarization.** This polarization is due to a reduction of the concentration of the ions determining the potential at the surface of the electrode in electrolysis.

Let us consider as an example the electrolysis of a solution of silver nitrate with a concentraton of $c^\circ$ g-mol/cm$^3$ in the presence of a considerable amount of $KNO_3$. A small silver wire is used as the cathode and a piece of a platinum sheet with a very great surface area as the anode. In the absence of a current the potential of the cathode can be calculated according to the Nernst equation [see Eq. (20.15)]

$$\varphi = \varphi^\circ + \frac{RT}{F} \ln c^\circ \tag{24.1}$$

Let us apply a small potential difference to the electrodes. The reduction of the silver ions to metallic silver begins at the cathode. Since the silver electrode is a reversible one, the reduction of the ions $Ag^+$ will proceed no matter how little the potential of the silver electrode will deviate from its equilibrium value when an external potential difference is applied. In the passage of a current, the concentration of the silver ions in direct proximity to the cathode decreases, while their concentration in the remaining part of the solution and at the surface of the anode remains constant. Thus a certain gradient of concentrations occurs that results in diffusion of the ions from the bulk of the solution to the surface of the electrode[1]. The latter acquires the potential $\varphi'$ corresponding to the new

[1] So as not to introduce complications, no account is taken of the fact that the motion of the discharging particles to the electrode also occurs under the influence of the electric field in the solution. Such motion is called *migration* in electrochemistry. Migration of both the ions discharging on the electrode and the undischarging ones occurs in an electrostatic field. If a large amount of the electrolyte (a background) is added to the solution and its ions are not reduced on the electrode, only an insignificant part of the current in the solution will be due to the migration of the particles being reduced, and it may be neglected. In the example being considered potassium nitrate is the background.

value of the concentration $c_s$ at its surface:

$$\varphi' = \varphi^\circ + \frac{RT}{F} \ln c_s \tag{24.2}$$

As the current continues to flow, the gradient of concentration at the cathode grows, and the supply of ions from the bulk of the solution by diffusion grows. After a certain time such conditions are created when the number of ions disappearing owing to the reaction becomes equal to the number of ions supplied to the surface of the electrode as a result of diffusion. A certain stationary, i.e. unchanging in time, distribution of the ions at the cathode sets in.

In stationary conditions the intensity of the current flowing through the solution is determined by the number of gramme-ions $n_i$ that diffuse to the electrode in a unit of time. According to Fick's law, this number is

$$n_i = DA \frac{c^\circ - c_s}{l} \tag{24.3}$$

where $D$ = diffusion coefficient of discharging ion
$l$ = thickness of layer in which the concentration drops from $c^\circ$ to $c_s$, i.e. the thickness of the diffuse layer
$A$ = surface area of electrode.

To calculate the intensity $I$ of the current flowing to the electrode it is necessary to multiply the quantity $n_i$ by $zF$, where $z$ is the number of electrons disappearing upon the reduction of one ion (the charge number), in the example being considered $z = 1$ for $AgNO_3$, and $F$ is the Faraday constant

$$I = zFDA \frac{c^\circ - c_s}{l} \tag{24.4}$$

An increase of the current is accompanied by a decrease in the value of $c_s$. When a certain maximum current, called the maximum diffusion current $I_d$, is reached, $c_s$ becomes equal to zero. Hence the maximum diffusion current is

$$I_d = zFDA \frac{c^\circ}{l} \tag{24.5}$$

From Eqs. (24.4) and (24.5) we have

$$c_s = c^\circ \left(1 - \frac{I}{I_d}\right) \tag{24.6}$$

Using the expression obtained for $c_s$ in Eq. (24.2) and subtracting Eq. (24.1) from the result, we find that the change in potential due to concentration polarization will be

$$\Delta\varphi = \frac{RT}{zF} \ln \left(1 - \frac{I}{I_d}\right) \tag{24.7}$$

Concentration polarization is observed in various processes of industrial electrolysis, in the operation of accumulators, etc.

The values of $\Delta\varphi$ of both electrodes add up into the *e.m.f. of concentration polarization* directed against the potential difference applied. This is why the latter must be increased by the e.m.f. of concentration polarization to obtain the current intensity required for electrolysis. Since currents of a quite great density are used in industrial electrolysis, considerable e.m.f.s of polarization occur caused by changes in the concentrations at the surface of the electrodes. This increases the consumption of electrical energy. For this reason the elimination or lowering of concentration polarization is an important practical problem. One of the principal ways of solving this problem is stirring of the solutions. Concentration polarization lowers the e.m.f. of chemical sources of current during their operation. This reduction can be avoided by creating special conditions of operation of the current sources or using saturated solutions of salts with an excess of the solid salt (the Weston cell).

The phenomena of concentration polarization on a dropping mercury electrode and the maximum diffusion current underlie the widely used polarographic method of analysis (see Sec. 24.12).

**24.4. Ideally Polarizable Electrodes. Electrochemical Polarization.** Substances decompose under the influence of an electric current only in definite conditions. In contrast to electronic conductors, electrolytes conduct a current and, consequently, decompose only at sufficiently high voltages. This contradicts Ohm's law in its customary form, according to which the current intensity in a circuit is always proportional to the voltage, i.e.

$$I = \frac{E}{R}$$

When a voltage is applied and then gradually increased, the intensity of the current in a cell remains insignificant until the voltage reaches a certain value. Now a growth in the current intensity is observed and electrolysis proper sets in. The current intensity grows especially sharply in electrolysis, during which solids or gases are liberated. Figure 24.1 shows graphically the relation between the current intensity and the voltage. Curve *1* characterizes a circuit containing electronic conductors and curve *2*, electronic and electrolytic conductors.

Let us attempt to explain the specific relation between the current intensity and the voltage observed when a current passes through an electrolyte. Let us immerse two platinum electrodes into an electrolytic bath filled with a solution of hydrochloric acid and connect them to a source of electricity so designed that the voltage supplied can be changed. At the initial moment (the external voltage is equal to zero) the potentials of both platinum electrodes are obviously

identical. When even a small voltage is applied, a current will flow between the electrodes in the external circuit. Electrons will flow from one electrode to the other. They cannot directly pass through an electrolyte, therefore if there are no electrochemical processes at the electrodes, the number of electrons will grow on one of them and decrease on the other. In other words, one of the electrodes will be charged negatively and the other positively. As a result the corresponding electrical double layers will change, and a potential difference will appear between the electrodes directed against the voltage supplied by the external source. This potential difference gradually increases and becomes equal to the potential difference applied from the external source. After this the current stops flowing. In the absence of an electrochemical process there will practically be no current, since a very small quantity of electricity is sufficient to change the charge of the double layer. In the example described above we observe polarization of the electrodes in the simplest form.

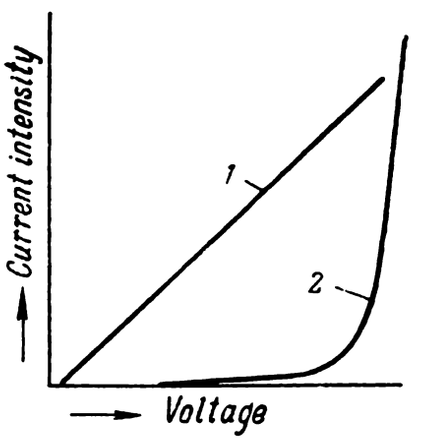



Fig. 24.1. Dependence of current intensity on voltage:
1 – in circuits with electronic conductors; 2 – in circuits with electronic and electrolytic conductors

High polarization is observed on metals (platinum, gold, mercury), in solutions of salts of alkali metals, for example on a mercury electrode that is immersed in a 0.1 $N$ solution of potassium chloride free of oxygen and other oxidizers. The mercury practically does not give up its ions to the solution which makes their liberation on the electrode impossible. The liberation of hydrogen from a neutral solution is possible only at a considerable negative potential of the electrode. The liberation of potassium from a 0.1 $N$ solution requires a still greater negative potential ($\varphi = -2.983$ V).

In the example considered above (mercury in a KCl solution), no electrical double layer is formed. When this electrode receives a certain charge from an external source, it acquires a certain potential that may change continuously as a result of the change in the charge supplied to it. The density of the charge on the surface of the electrode continuously changes, but there is no electrochemical process. The electrode retains this property only within a certain interval of values of the potential. Electrodes of this kind are called *ideally polarizable ones.*

Thus, in the absence of an electrochemical process, the passage of electricity through the electrolyte results in a purely physical process of charging of the electrodes, i.e. in a change of their potentials. An e.m.f. appears directed against the external voltage, and the current stops flowing.

Polarization of the electrodes also occurs in the presence of electrode processes. However, the easier the metal electrode exchanges ions with the solution (the greater the exchange current), the less is the polarization. Thus, an increase in the negative charge of an electrode (displacement of its potential in a negative direction) will immediately lead to the liberation of a certain number of metal cations from the solution, which bind the electrons of the metal and displace the electrode potential in the positive direction. A metal electrode immersed in a solution of a salt of the same metal is only slightly polarized.

When a greater voltage is applied, further charging of the electrodes and changing of their potential occurs. It will continue until polarization results in the appearance of electrochemical processes accompanied by the consumption and reception of electrons. Now electrolysis in the full meaning of this word will begin, and a stationary (unchanging) current will flow through the system. In this case electrochemical (chemical) polarization manifests itself completely. Its e.m.f. is directed against the potential difference applied from the external source.

Thus, in a solution of hydrochloric acid, only a single electrode process connected with the consumption of electrons can appear on the negatively charged electrode (cathode), namely the process of discharging of the hydroxonium ions:

$$2H_3O^+ + 2e \rightarrow 2H_2O + H_2(\text{ads. on Pt}) \rightarrow 2H_2O + H_2\,(\text{gas})$$

This reaction is characteristic of a hydrogen electrode. A quite definite potential, conventionally assumed to be equal to zero, corresponds to equilibrium between the ions $H_3O^+$ (at $a_+ = 1$) and the molecular gaseous hydrogen ($p = 1$ atm). At this potential there is equilibrium of a dynamic nature, i.e. both the process of discharge of the hydroxonium ions and the process of ionization of the adsorbed hydrogen simultaneously proceed at the electrode-solution interface, and the processes of adsorption and desorption of hydrogen at the electrode-gas interface. The rates of the opposite processes are equal. If a hydrogen electrode is polarized cathodically, i.e. electrons are supplied to it, equilibrium will be violated and discharge of the hydroxonium ions will mainly occur. Hence it is clear that discharge of the hydroxonium ions and liberation of the molecular hydrogen will be observed only when an equilibrium potential of the hydrogen electrode is reached that corresponds to the activity of the hydroxonium ion in the solution and to the pressure of the liberated $H_2$ (in the absence of overvoltage). It is this factor that determines the maximum polarization of the cathode in electrolysis with the liberation of hydrogen.

In the electrolysis of hydrochloric acid, chlorine is liberated at the anode when a definite potential is reached. A potential of the

chlorine electrode depending on the concentration of $Cl^-$ in the solution should correspond to this process ($\varphi^\circ_{Cl^-} = 1.36$ V at $a_{Cl^-} = 1$ and $p_{Cl_2} = 1$ atm).

Thus the reason why Ohm's law in its usual form cannot be applied to electrolytes is the reversely directed e.m.f. of electrode polarization. Hence, when a circuit contains an electrolyte, this law should be written in a somewhat altered form:

$$I = \frac{E - E_p}{R}$$

where $E_p$ is the e.m.f. of polarization.

The maximum value of this quantity for definite conditions (the activity of the corresponding ions must be known) can be calculated with the aid of tables of standard potentials corresponding to the electrode processes occurring, and of the Nernst equation

$$E_p = \varphi_1 - \varphi_2 = \varphi_1^\circ - \varphi_2^\circ + \frac{RT}{z_+F} \ln a_+ + \frac{RT}{z_-F} \ln a_-$$

It is assumed here that the concentration polarization has been reduced to zero and $c_s = c^\circ$.

For example, in the electrolysis of HCl, aq, the e.m.f. of polarization should equal that of a chlorine-hydrogen electrochemical cell (i.e. a cell with a chlorine and a hydrogen electrodes). The value of the e.m.f. of this cell depends on the concentration of the solution and the conditions of liberation of gaseous hydrogen and chlorine. Thus at the electrodes (if overvoltage of the $H_2$ and $Cl_2$ is absent—see Sec. 24.6) at $a_{HCl} = 1$ and $p = 1$ atm we have

$$E_p = \varphi^\circ_{Cl_2 \mid Cl^-} - \varphi^\circ_{H_2 \mid H^+} = 1.36 - 0 = 1.36 \text{ V}$$

Consequently, the decomposition of substances by electrolysis occurs only at a definite voltage characteristic for the given solution and electrodes. This voltage depends on the concentration of the solution.

**24.5. Decomposition Voltage.** The minimum potential difference that must be created between electrodes for electrolysis to begin is called the *decomposition voltage* of the electrolyte. This quantity is obviously equal to the sum of the *discharge potentials* of the ions on the electrodes. In the absence of an overvoltage (see the following section) on the electrodes, the decomposition voltage is equal to the sum of the equilibrium potentials of the electrodes formed after the beginning of electrolysis (in the above example—the electrolysis of HCl, aq—it is equal to the sum of the equilibrium potentials of the chlorine and hydrogen electrodes). When there is an overvoltage even on one electrode, the decomposition voltage is greater than the sum of the equilibrium potentials.

The value of the decomposition voltage can be determined for a given electrolyte having a definite concentration more or less accurately only if pure solids are liberated on the electrodes. If solid or liquid solutions are formed on the electrodes in electrolysis and, especially, if gases are liberated on them, the decomposition voltage depends on the shape and dimensions of the electrodes, the nature of their surface, the conditions of removal of the gases and many other factors that frequently cannot be taken into account. For this reason the value of the decomposition voltage cannot serve as a single-valued characteristic for any electrolyte in different conditions, the same as the values of the ion discharge potentials. The value of the e.m.f. of electrochemical polarization in electrolysis reflects the e.m.f. that actually appears when an external potential difference is applied and counteracts electrolysis, regardless of whether electrolysis is proceeding or it has been suppressed by the e.m.f. of electrochemical polarization. In a particular case the maximum polarization of electrodes may be only insignificantly lower than the applied potential difference. In this case this difference is equal to the sum of the ion discharge potentials (the decomposition voltage).

It is clear from the above that the minimum value of the decomposition voltage should be equal to the e.m.f. of polarization.

The values of the e.m.f.s of polarization in the electrolysis of selected substances are given in Table 24.1.

TABLE 24.1

**Maximum E.M.F. of Polarization in the Electrolysis of Solutions of Selected Substances**

| Electrolyte | Maximum e.m.f. of polarization, V | Electrolyte | Maximum e.m.f. of polarization, V |
|---|---|---|---|
| $H_2SO_4$ | 1.67 | $AgNO_3$ | 0.70 |
| $HNO_3$ | 1.69 | HCl 2 *N* | 1.26 |
| $H_3PO_4$ | 1.70 | HCl 1 *N* | 1.31 |
| NaOH | 1.69 | HCl 0.5 *N* | 1.34 |
| KOH | 1.67 | HCl 1/6 *N* | 1.41 |
| $NH_4OH$ | 1.74 | HCl 1/16 *N* | 1.62 |
| $Na_2SO_4$ | 2.21 | HCl 1/32 *N* | 1.69 |
| $ZnSO_4$ | 2.35 | | |

A glance at Table 24.1 shows that the e.m.f.s of polarization in the electrolysis of oxygen-containing acids and alkalies of medium concentrations on platinum electrode are close in value. Since these quantities characterize the free energy required for the electro-

lysis of solutions of various substances, it is apparent that identical processes proceed both at the cathode and at the anode in the electrolysis of a whole series of substances. Indeed, in these solutions hydrogen is liberated at the cathode, and oxygen at the anode. In solutions of acids the liberation of hydrogen at the cathode obviously follows the scheme

$$2H_3O^+ + 2e \rightarrow 2H_2O + H_2$$

i.e. the hydroxonium ions become discharged. In solutions of alkalies the discharge of hydroxonium ions, and not ions of the alkali metal, takes place. However, owing to the insignificant concentration of the $H_3O^+$ at a high intensity of the current mainly carried by ions of the alkali metals, the approach to the electrode of sufficient quantities of hydroxonium ions and the liberation of considerable amounts of hydrogen cannot be ensured. Hydrogen is apparently liberated from a solution of an alkali by the direct decomposition of water molecules adsorbed on the electrode:

$$2H_2O + 2e \rightarrow 2OH^- + H_2$$

It was previously assumed that the liberation of hydrogen from solutions of alkalies and salts of alkali metals follows a different scheme, for example for KOH, aq

$$2K^+ + 2e \rightarrow 2K$$
$$2K + 2H_2O \rightarrow 2KOH + H_2$$

i.e. first the ions of the alkali metal discharge, and then the atoms of this metal formed interact with water with the formation of an alkali and hydrogen. It was thus assumed that the liberation of hydrogen is the result of a secondary process—the chemical interaction of the alkali metal with water. This assumption does not correspond to what actually occurs. Since there is an aqueous solution, two species of cations are present in the electrolyte (for example, in a solution of KCl they are $K^+$ and $H_3O^+$). When the potential of the electrode changes in a negative direction, the discharge potential of the hydroxonium ions is first reached, which in a neutral solution at $p = 1$ atm is equal to only —0.4 V, and the process of liberation of gaseous hydrogen described above begins.

Discharge of the potassium ions, as can be seen from Table 20.1, can occur only at high negative potentials (at $a_{K^+} = 1$ only at a potential of —2.9 V), which in the electrolysis of aqueous solutions is in general impossible, since at a much lower voltage (1.3-1.7 V) depending on the concentration of the acid, the liberation of $H_2$ and $O_2$ begins.

The liberation of oxyge from alkaline solutions can be the result of the only possible electrode reaction—discharge of the hydroxyl

ions at the anode:

$$4OH^- - 4e = 2H_2O + O_2$$

In the electrolysis of acids, where the concentration of the hydroxyl ions is very low, oxygen is liberated as a result of the direct decomposition of the water molecules at the anode:

$$6H_2O - 4e = 4H_3O^+ + O_2$$

At high potentials ($\varphi$ = 2.5-3 V) other anode processes may proceed. For example in the electrolysis of solutions of perchloric acid, the liberation of oxygen from the molecules of $HClO_4$ begins.

It was previously assumed that in solutions of oxygen-containing acids or their salts the corresponding anions discharge, and the liberation of oxygen is the result of the interaction of the radicals of these anions with water. For example:

$$2SO_4^{2-} - 4e = 2SO_4$$

$$2SO_4 + 6H_2O = 2SO_4^{2-} + 4H_3O^+ + O_2$$

This assumption is not correct. The ions $OH^-$ have the smallest discharge potential (+1.23 V), and for this reason in the electrolysis of such salts the liberation of oxygen is due to the discharge of hydroxyl ions.

In solutions of an alkali, where the concentration of $H_3O^+$ is very low, its discharge potential is a negative quantity (about 0.8 to 1 V).

Thus, in the electrolysis of acids, alkalies and the relevant salts of alkali and alkaline-earth metals, a single process of decomposition of water takes place at the electrodes. In other words, the liberation of hydrogen and oxygen is a primary process in electrolysis. The role of the remaining ions consists only in ensuring an electrical conductance sufficient for electrolysis. It should be underlined that the close values of the e.m.f.s of polarization in the electrolysis of oxygen-containing acids and alkalies are observed only when electrodes of definite metals (Pt, Pd) are used on which the overvoltage of hydrogen is low.

For solutions of other substances the e.m.f. of polarization is a specific quantity, which points to the different nature of electrode processes for different substances.

In solutions of salts of metals that are less electronegative than hydrogen, the metal may be liberated (deposited) on the cathode. In the electrolysis of acids (not containing oxygen) and their salts, the corresponding anions discharge, as a rule, at the anode.

It is interesting to note the behaviour of hydrochloric acid. In concentrated solutions chlorine is liberated at the anode, and in dilute ones oxygen, and the e.m.f. of polarization changes (Table 24.1). With dilution of the acid, the activity of the chloride ions

decreases, and in accordance with formula (11.14a) the equilibrium potential of the chlorine electrode becomes more positive than the potential of discharge of the $OH^-$ ions. It is for this reason that the anode process changes, namely, the discharge of the chloride ions appreciably decreases, and discharge of the hydroxyl ions or water molecules and the liberation of oxygen take place.

**24.6. Overvoltage.** When electrochemical polarization of the electrodes of an electrolytic cell occurs, electrolysis can begin at a potential difference applied from an external source equal to (more exactly, very insignificantly exceeding) the e.m.f. of electrochemical polarization. The latter is equal to the difference between the reversible potentials of the electrodes of the cell (the discharge potentials of the ions).

Frequently, however, for electrolysis to begin it is necessary that the potential difference applied be greater by a finite value than the difference of the equilibrium potentials across the electrodes in electrolysis. As indicated above, this minimum value of the potential difference applied from an external source is called the *decomposition voltage.* The difference between the decomposition voltage and the sum of the equilibrium potentials on the electrodes is called the *overvoltage* (*overpotential*).

Thus, for liberation of an anion on the anode, the potential $\varphi = \varphi_A + \eta_A$ (where $\varphi_A$ is the equilibrium potential on the anode and $\eta_A$ is the overvoltage on the anode) is required. For liberation of a cation on the cathode, the potential $\varphi' = \varphi_C + \eta_C$ (where $\varphi_C$ is the equilibrium potential on the cathode and $\eta_C$ is the overvoltage on the cathode) is required. Hence the overvoltages on the electrodes are

$$\eta_A = \varphi - \varphi_A$$

$$\eta_C = \varphi' - \varphi_C$$

The magnitude of the overvoltage on an electrode depends on the nature of the electrode, the density of the current, the composition of the solution and other factors. The sum of the overvoltages on the anode and cathode for a definite electrochemical process in a cell is equal to the excess voltage that must be applied to the electrolytic bath above its equilibrium e.m.f. for electrolysis to begin. The excess voltage, in addition to the overvoltage on the electrodes, also includes the ohmic voltage drop in solution corresponding to its electric resistance.

The magnitude of the overvoltage is different for different electrochemical processes. Thus, the overvoltage of hydrogen on a mercury electrode at a current density of $j = 10^{-4}$ A/cm$^2$ is equal to 0.94 V. In connection with the great practical significance of the reaction of liberation of hydrogen for a number of industrial proces-

ses (the electrolysis of water, chlorine electrolysis, the operation of accumulators and galvanic cells, corrosion), this electrochemical reaction and the corresponding overvoltage have been studied in the greatest detail.

The fact that the concentration of adsorbed hydrogen increases in electrolysis to above the equilibrium value has been experimentally proved for a number of metals (Ni, Fe, Pd).

I. Tafel (1905) empirically deduced an equation that relates the overvoltage to the density of the current passing through a solution,

TABLE 24.2

**Values of Constants *a* and *b* of Tafel Equation for the Reaction of Cathode Liberation of Hydrogen on Selected Metals at $t = 20$ °C**

| Metal | Solution | *a* | *b* |
|---|---|---|---|
| Lead | $H_2SO_4$, 1.0 *N* | 1.533 | 0.118 |
| Thallium | $H_2SO_4$, 1.7 *N* | 1.55 | 0.140 |
| Mercury | $H_2SO_4$, 5.0 *N* | 1.400 | 0.116 |
| Ditto | HCl, 1.0 *N* | 1.390 | 0.119 |
| Ditto | KOH, 0.1 *N* | 1.430 | 0.093 |
| Cadmium | $H_2SO_4$, 1.7 *N* | 1.450 | 0.120 |
| Zinc | $H_2SO_4$, 1.0 *N* | 1.24 | 0.118 |
| Tin | HCl, 1.0 *N* | 1.24 | 0.116 |
| Copper | HCl, 0.1 *N* | 0.790 | 0.117 |
| Silver | HCl, 1.0 *N* | 0.320 | 0.060 |
| Ditto | HCl, 5.0 *N* | 0.470 | 0.070 |
| Iron | HCl, 1.0 *N* | 0.770 | 0.130 |
| Ditto | NaOH, 4.8 *N* | 0.350 | 0.070 |
| Nickel | NaOH, 0.11 *N* | 0.64 | 0.100 |
| Cobalt | HCl, 1.0 *N* | 0.62 | 0.140 |
| Palladium | KOH, 0.1 *N* | 0.637 | 0.125 |
| Tungsten | HCl, 1.0 *N* | 0.23 | 0.040 |
| Ditto | HCl, 5 0 *N* | 0.550 | 0.110 |
| Smooth platinum | HCl, 1.0 *N* | 0.10 [1] | 0.13 [1] |
| Ditto | $\left\{ + \begin{matrix} \text{NaOH, 1.0 } N \\ Na_2SO_4\text{, 1.0 } N \end{matrix} \right\}$ | 0.31 [1] | 0.197 [1] |
| Ditto | HCl, 1.0 *N* | 0.3 [2] | 0.14 [2] |
| Platinum | HCl, 0.5 *N* | 0.073 | 0.028 |

[1] Corrected by concentration polarization.
[2] At $j > 1$ A/cm$^2$.

i.e. to the rate of an electrochemical process[1]:

$$\eta = a + b \log j \tag{24.8}$$

where $\eta$ = overvoltage, V
$j$ = current density, A/cm²
$a$ and $b$ = constants.

The meaning of the constant $a$ is clear—if $j = 1$ A/cm², then $\eta = a$. Consequently, the quantity $a$ gives the value of the overvoltage on different metals at a density of the electric current equal to 1 A/cm². It appreciably depends on the material of an electrode. Thus, for a platinum electrode $a = 0.3$ V, and for a lead one $a = 1.56$ V (Table 24.2).

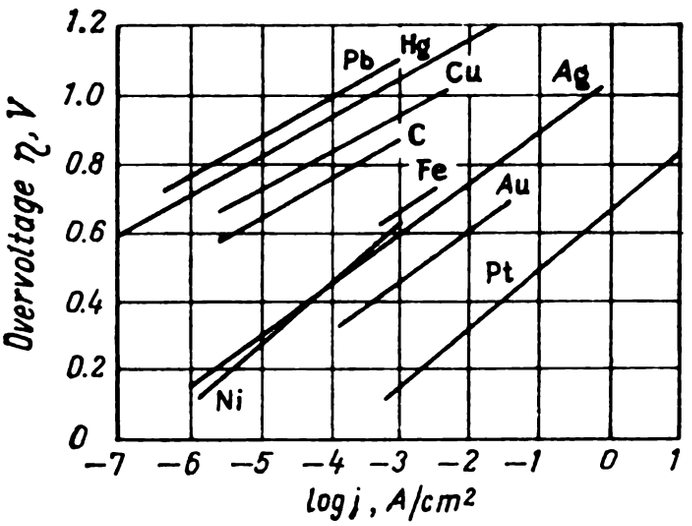



Fig. 24.2. Hydrogen overvoltage on selected metals

The constant $b$ only slightly depends on the material of an electrode and is a characteristic of the electrochemical process itself. It is approximately equal to $2 \times 2.30 \times RT/zF$, i.e. to 0.116 V at $z = 1$ and room temperature. This means that when the current density grows ten times, the overvoltage increases by 0.116 V. Figure 24.2 shows the overvoltage of hydrogen $\eta$ versus the logarithm of the current density on selected electrodes. It can be seen quite well that the Tafel equation corresponds to experimental data within a very broad range of values of $j$ and that the values of $b$ are close for different metals in aqueous solutions. The same values of $b$ are also observed for metals immersed in a solution in methyl alcohol and ether.

The Tafel equation is naturally not applicable at very low current densities, since it follows from Eq. (24.8) that $\eta = -\infty$ at $j = 0$, while actually $\eta = 0$ at $j = 0$.

An explanation showing why this equation cannot be applied at very low densities of the total current and, therefore, at low values of $\eta$, is given on a later page (see p. 588).

**24.7. Theories of Hydrogen Overvoltage.** Overvoltage in principle is a result of the relatively low rate of an electrochemical process.

[1] A. Shlygin deduced an equation for the kinetics of electrode processes whose feature is not only the absence of the constants $a$ and $b$, but also the presence of an exchange current, which makes this equation a general one (see *Zhurnal fizicheskoi khimii*, 39, 3069, 1965).

Electrochemical reactions are complicated processes with consecutive steps, and a low rate of any of them results in the violation of equilibrium and appearance of an overvoltage. Let us consider these steps for the hydrogen overvoltage[1].

The discharge of hydroxonium ions leading to the liberation of molecular hydrogen seems to be a very simple electrode reaction, but it actually is a quite complicated one, since it consists of a number of consecutive steps:

1. *Diffusion Step.* The electrochemical process proceeds on an electrode. For this reason the $H_3O^+$ ions must be rapidly supplied to its surface. This is accomplished by migration of the ions and their diffusion.

2. *Dehydration Step.* In a hydroxonium ion the proton is firmly bound to a molecule of water, and the discharge of hydroxonium is impossible without preliminary dehydration: $H_3O^+ \rightarrow H^+ + H_2O$.

3. *Step of Discharge and Adsorption of a Proton.* This is the electrochemical process proper: $H^+ + e \rightarrow H$. The hydrogen atoms formed are simultaneously adsorbed by the metal: $H + Me \rightarrow$ $\rightarrow Me \mid H$ (ads.). It is possible that steps 2 and 3 are combined in one act—discharge of the hydroxonium ions.

4. *Molization or Recombination Step.* When the surface of the electrode is saturated, the adsorbed hydrogen molizes and passes into the solution: $2H$ (ads.) $\rightarrow H_2$ (solut.).

5. *Gas Liberation Step.* The hydrogen molecules formed supersaturate the solution and are liberated in the form of gas bubbles: $H_2$ (solut.) $\rightarrow H_2$ (gas).

In cathode polarization electrons pass to the electrode, and a decrease in the rate of any step automatically results in a growth of the cathode potential.

The theories of overvoltage differ in the step considered to be the slowest one and, consequently, limiting the rate of the summary electrochemical process. Thus, according to C. Müller the rate of the last step (formation and liberation of the gaseous phase) is the slowest one; according to M. Le Blanc it is the dehydration step; according to A. Smits—the step of ion discharge; according to Tafel—the process of molization; and according to Nernst—the adsorption step.

Some of these theories are only of a historical interest, and therefore let us consider only the ones of them that have retained their significance to date.

Any theory must be proved experimentally. For this reason, naturally, the correctness of a theory of overvoltage is determined by the possibility of using this theory to explain the Tafel equation, which

[1] A great number of investigations have been devoted to the hydrogen overvoltage; several theories have been proposed to explain this phenomenon.

is based on experimental data. All the theories, however, with certain assumptions result in the Tafel equation.

For example, this equation can be derived on the basis of the recombination theory, which Tafel himself did in his time.

*Recombination Theory.* For a long time this theory of overvoltage, proposed by Tafel back in 1905, was the most popular one. The slowest step according to it is that of molization of the adsorbed hydrogen. Hence in the process of electrolysis the concentration of atomic hydrogen on the surface increases in comparison with the equilibrium concentration with the molecular hydrogen (gas). This leads to displacement of the electrode potential in the negative direction.

Indeed, according to the equation

$$H\ (ads.) + H_2O \rightarrow H_3O^+ + e$$

the increase in the concentration of the adsorbed hydrogen displaces electrode equilibrium to the right. The rate of ionization of the hydrogen grows. Since the electrons remain on the electrode, the negative charge, and, therefore, potential of the latter increase.

The rate of recombination of the hydrogen atoms into molecules is proportional to the square of the surface concentration [H] of the hydrogen adsorbed on the metal

$$\frac{\Delta n_{H_2}}{\Delta t} = k'\,[H]^2 \tag{24.9}$$

On the other hand, the rate of electrochemical liberation of hydrogen is equal to[1]

$$\frac{\Delta n'_{H_2}}{\Delta t} = \frac{1}{2F} I \tag{24.10}$$

If the molization step is the limiting one in the electrochemical liberation of hydrogen, i.e. the rate of molization of hydrogen is considerably lower than those of the other steps in the liberation of hydrogen, then $\Delta n_{H_2}/\Delta t = \Delta n'_{H_2}/\Delta t$, and it follows from Eqs. (24.9) and (24.10) that

$$\frac{I}{F} = 2k'\,[H]^2 = k\,[H]^2 \tag{24.11}$$

Since the overvoltage is due to the increase in the concentration of the adsorbed hydrogen, then according to Tafel

$$\eta = \varphi - \varphi_R = \frac{RT}{F}\ln[H] + \text{const} - \left(\frac{RT}{F}\ln[H_e] + \text{const}\right) = \frac{RT}{F}\ln\frac{[H]}{[H_e]}$$

[1] Since the current intensity $I$, i.e. the quantity of electricity flowing in a unit of time, is equal to the product of the number of moles of hydrogen liberated in a unit of time and $2F$ ($z = 2$), i. e.

$$\frac{\Delta n'_{H_2}}{\Delta t} 2F = I$$

where $[H_e]$ is the surface concentration of the atomic hydrogen on an electrode upon equilibrium of this hydrogen with the molecular hydrogen in the gaseous phase.

Let us substitute for [H] in the last equation its value from Eq. (24.11). Hence

$$\eta = \frac{RT}{F} \ln \frac{k\sqrt{I}}{[H_e]} \tag{24.12}$$

where $k = \frac{1}{(2k'F)^{1/2}}$.

Since $k$ and $[H_e]$ are constant quantities, the equation is easily reduced to the form

$$\eta = a + \frac{RT}{2F} \ln I \tag{24.13}$$

or finally

$$\eta = a + 0.029 \log I \tag{24.13a}$$

It can be seen that the equation properly reflects the experimentally found semilogarithmic relation (the Tafel equation) between the overvoltage and the current intensity. On the basis of the above derivation, however, the value of $b$ is found to be equal to 0.029, and not to 0.116, i.e. it is only one-fourth of the experimental value, which is a serious shortcoming of Tafel's theory.

This theory was further developed by a number of scientists. N. Kobozev related the retardation of the molization of hydrogen to the energy of adsorption of the hydrogen by a metal.

In deducing his equation Tafel did not take into account the heterogeneous nature of the surface and the repulsive forces between the adsorbed atoms. If this is done, the value of the coefficient $b$ grows and upon certain assumptions may reach 0.116. Thus the main shortcoming of the theory—the low value of $b$—can be eliminated.

The recombination theory explained for the first time the influence of the material of the electrode on the magnitude of the hydrogen overvoltage.

*Theory of Slow Discharge of Ions.* Recent times have seen general acknowledgement of this theory. According to it the process of discharge of the ions is the slowest step of the complicated electrochemical process. Although this idea was put forward long ago (Smits), it was not acknowledged for a long time, since it seemed very improbable that ions may discharge slowly. This theory attracted due attention only after the investigations of T. Erdey-Gruss and M. Volmer (1930) who assumed, in particular, that the discharge of ions also requires a considerable activation energy and for this reason may proceed at a low rate.

On the basis of this assumption, Volmer succeeded in deducing the Tafel equation. Let us consider this deduction.

Let us apply to an electrochemical process the usual equation for the rate of a chemical process, namely,

$$J = k' [H_3O^+] e^{-E/RT} \tag{24.14}$$

where $E$ is the activation energy of the process.

Since the rate of an electrochemical process is determined by the current intensity

$$It = zFn: \quad I\Delta t = zF\Delta n \text{ and } J = \frac{\Delta n}{\Delta t} = \frac{I}{zF}$$

then for the current intensity $I$ we can write

$$I = k'' [H_3O^+] e^{-E/RT} \tag{24.14a}$$

From Eq. (24.14a) for a solution having a constant composition we get

$$I = ke^{-E/RT} \tag{24.14b}$$

The part played by the overvoltage consists in reducing the activation energy. The magnitude of the reduction is proportional to the overvoltage. Assume that it is equal to $\alpha F\eta$ (here $\alpha$ is a proportionality factor). Hence

$$E = E_0 - \alpha F\eta \tag{24.15}$$

where $E_0$ is the activation energy of an unpolarized electrode.

Thus, in the presence of an overvoltage

$$I = ke^{-(E_0-\alpha F\eta)/RT} \text{ and } I = ke^{-E_0/RT}e^{\alpha F\eta/RT} = k_1 e^{\alpha F\eta/RT}$$

Taking logarithms, we get

$$\ln I = \ln k_1 + \frac{\alpha F\eta}{RT} \tag{24.15a}$$

Solving Eq. (24.15a) with respect to $\eta$ we get

$$\eta = \frac{RT}{\alpha F} \ln I - \frac{RT}{\alpha F} \ln k_1 \tag{24.16}$$

Let us change over from the current intensity $I$ to the current density $j$, inserting $I = jA$. Assuming that $A$ (the surface area of an electrode) is constant, passing over to common logarithms and denoting the sum of the addends that are constant at a given temperature by $a$, we get the Tafel equation (24.8):

$$\eta = a + \frac{RT}{\alpha F} \ln j = a + \frac{0.058}{\alpha} \log j$$

If $\alpha = 0.5$, then $b = 0.058/\alpha = 0.116$.

A merit of the theory of slow ion discharge is the fact that the derivation of the Tafel equation based on this theory results in a correct value for the coefficient $b$ when a certain assumption is made ($\alpha = 0.5$).

It is necessary to find out why a change in the potential, i.e. the appearance of an overvoltage, results in an increase in the rate of discharge.

The electrical double layer on platinum of a reversible hydrogen electrode is so constructed that the surface of the platinum is charged negatively, while the external surface of the double layer is formed by hydroxonium ions. In cathodic polarization, i.e. when electrons are supplied to the surface of an electrode, the hydroxonium ions approaching this surface do not discharge immediately, but are first included in the double layer. As a result the surface density of the charge of the double layer and the potential of the electrode grow. This leads to stretching of the bonds between a proton and a molecule of water, i.e. to deformation of the hydroxonium ion and its activation.

Upon further polarization, this deformation of the hydroxonium ions increases, and finally the proton breaks away from the water molecule and instantaneously becomes neutralized, and the hydrogen atoms formed are adsorbed on the metal.

Hence, the activation energy is necessary for dehydration of the proton.

The theory of slow discharge, like other modern theories by the way, easily explains the inapplicability of the Tafel equation at low polarization of an electrode (at low values of the current intensity).

The equation $I = ke^{-E/RT}$ is true only on condition that the process proceeds in one direction, i.e. either electrical reduction or electrical oxidation takes place.

In electrolysis, however, an exchange current remains that is the reverse in direction to the current passed through the cell (see Sec. 24.2). It is therefore also necessary to take into account the process which is the reverse of electrolysis when the reverse current has an appreciable value, and use the following equation instead of Eq. (24.14):

$$I = k_1 e^{-E_1/RT} - k_2 e^{-E_2/RT} \tag{24.17}$$

where the subscripts 1 and 2 relate to the forward and reverse processes, respectively.

Analysis of this equation shows that near the equilibrium potential (at a low overvoltage) the plot of $I$ against $\eta$ should be linear.

In the polarization of an electrode, i.e. when its negative potential grows, the rate of the forward process should grow, and that of the reverse one should decrease. At a certain overvoltage the latter becomes so small that it may be neglected. In this case the equation $I = k_1 e^{-E_1/RT}$ and, therefore, the Tafel equation becomes true.

Thus, in the liberation of hydrogen, the value of the overvoltage

required for practically complete stopping of the reverse process is several scores of millivolts.

To illustrate the part played by the reverse process, it is good to use the method of potential curves.

Figure 24.3 shows potential curves for a hydrogen atom (*bb*) and hydroxonium ion (*aa*) adsorbed on an electrode depending on the distance $x$ from its surface. In position $A$ the energy of the adsorbed hydroxonium is minimum. When the hydroxonium travels from point $A$ to $B$, its energy grows until the point of intersection of *aa* and *bb* is reached. After this point is passed, the proton receives an electron from the electrode, separates from the molecule of $H_2O$ and transforms into an adsorbed atom of hydrogen, approaching the equilibrium state at point $B$. The magnitude of the activation energy $E_1$ of hydroxonium discharge is shown in the figure. For the reaction of ionization of a hydrogen atom, the activation energy is equal to $E_2$ (the difference between the energies at points $C$ and $B$).

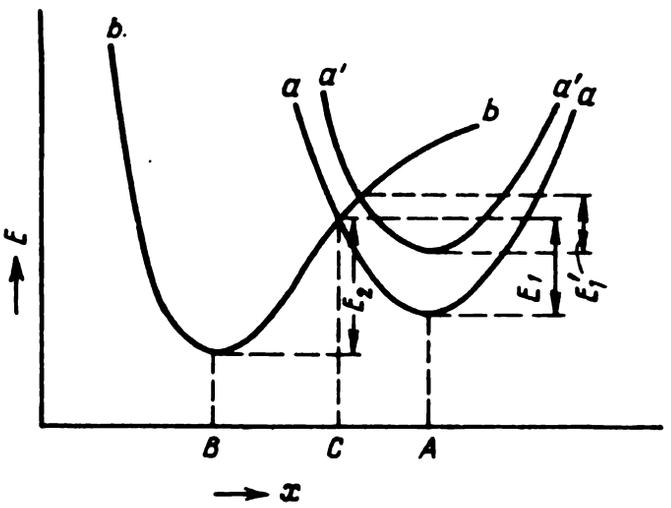



Fig. 24.3. Displacement of potential curve for hydrogen (hydroxonium) ion when electrode potential changes

Polarization of the electrode in the negative direction shifts curve *aa* to the position *a'a'* (the energy of the hydroxonium increases). The position of curve *bb* does not change, since the hydrogen atom is not charged. A glance at the figure shows that the activation energy of hydroxonium discharge in the new energy state ($E_1'$) becomes less.

Using similar potential curves for a hydrogen atom adsorbed on various solid surfaces, we can easily see that the overvoltage will decrease as the energy of adsorption of the hydrogen on the metal grows. An increase in the energy of adsorption results in dropping of the potential curve for an adsorbed atom. As follows from the figure, this leads to falling off of the activation energy of discharge.

The theory of slow discharge as set out by Volmer did not take into account the structure of the electrode-solution interface. For this reason it could not explain the influence of the composition of the electrolyte on the magnitude of the hydrogen overvoltage. The influence of the structure of the electrical double layer on the kinetics of electrochemical reactions was first taken into consideration by A. Frumkin. He showed that on one hand the forces of electrostatic interaction between an electrode and ions induce a change in

the concentration of the reacting ions in the reaction zone, and on the other the double layer influences the magnitude of the activation energy of the electrode process.

Since in the course of an electrochemical reaction a discharging ion should be adsorbed on the surface of the electrode, i.e. be in the Helmholtz layer (see Fig. 20.1), the concentration of the hydrogen ions in the surface layer $[H_3O^+]_s$ can be related to their concentration in the bulk of the solution $[H_3O^+]_0$ by the following equation:

$$[H_3O^+]_s = [H_3O^+]_0 \, e^{-F\psi_1/RT} \tag{24.18}$$

where $\psi_1$ is the potential of the metal together with the Helmholtz layer with respect to the solution. It is this surface concentration of the hydrogen ions that should be inserted into Eq. (24.14a).

At the same time the change in the energy of an adsorbed ion in polarization obviously depends not on the total potential jump $\varphi$ between the electrode and the solution, but on the value of $\varphi - \psi_1$. Thus the relation between the activation energy of the process of discharge and the potential and overvoltage, with account taken of the structure of the double layer, is expressed by the equation

$$E = E_0 + \alpha F \, (\varphi - \psi_1) = E_0 - \alpha F \eta - \alpha F \psi_1 \tag{24.19}$$

and not by Eq. (24.15). The above more precise definitions of the theory of slow discharge made it possible to explain the great amount of experimental data obtained by Soviet electrochemists on how the composition of a solution affects the value of the hydrogen overvoltage, and also the kinetics of other electrode processes, in particular the kinetics of the reactions of electrical reduction of anions.

At present the application and the significance of both the recombination and the slow discharge theories are quite clear.

The theory of slow discharge, which helps us to explain most of the phenomena associated with changes in the hydrogen overvoltage, is applicable to metals characterized by great values of the overvoltage (a low energy of hydrogen adsorption), for example Hg and Pb.

The theory of recombination is best applied to metals characterized by a low value of the overvoltage (a high energy of hydrogen adsorption), for example Pt and Ni.

The unsubstantiated nature of attempts to make one of the theories a general one can be shown by concrete consideration of the properties of a metal surface.

The real surface of solid metals has a sharply expressed heterogeneity both from the geometrical and the energy viewpoints. Owing to such heterogeneity, the energy of adsorption of hydrogen on the surface of an electrode will appreciably change upon transition from one adsorption centre to another one. Thus, on platinum the differences in the adsorption energy on different centres may exceed 10 kcal.

Consequently, the rate of discharge of the hydroxonium ions, and also the rate of molization on different parts of the surface may differ. For this reason there may also be different limiting steps on different parts of the surface of the same electrode during the same

electrochemical process. The truth of this statement was proved in studying the overvoltage of hydrogen on nickel.

The appearance of an overvoltage is a general phenomenon for electrochemical processes, since considerable overvoltages appear in the electrolytic liberation not only of hydrogen, but also of other gases, and of certain metals.

The process of electrochemical liberation of oxygen is of great theoretical and practical interest. As a result of the high chemical activity of the oxygen, complications are introduced into this process by the formation of various oxides on metals, even on platinum. For this reason gaseous oxygen is liberated from an oxidized surface. The fact that to date there is still no sufficiently substantiated theory of oxygen overvoltage is obviously explained by the complicated nature of the process of oxygen liberation. The most authentic is the assumption that the slowest step (the limiting one) is the decomposition of higher metal oxides of a variable composition according to the equation

$$Me_xO_y \longrightarrow Me_xO_{y-2} + O_2$$

In a number of cases, however, it has been proved that the slowest step is the process of formation of these oxides, i.e. the discharge of the hydroxyl ions.

Overvoltage is a problem whose solution has not only theoretical, but also a great practical significance. An overvoltage results in considerable amounts of electrical energy being consumed unproductively in industrial electrolysis. Hence the reduction of the overvoltage on electrodes is one of the most important tasks of applied electrochemistry. It is impossible to solve this problem without establishing the true mechanism of a complicated electrochemical process, without establishing its limiting step whose low rate leads to the appearance of an overvoltage. For this reason the task of electrochemical kinetics consists in finding ways of increasing the rate of this slowest step. It is clear that both the solution of the problem of overvoltage and in general the development of a modern theory of electrode processes are impossible without determining the true mechanism of the elementary acts forming a complicated electrochemical process.

**24.8. Electrodeposition of Metals.** Processes of the electrodeposition of metals have a great practical significance. The possibility of the technical application of these processes, namely, galvanoplastics, was discovered by B. Jacobi back in 1837. To date, however, the kinetics of the electrodeposition of metals has been studied comparatively little. This is explained by the experimental difficulties encountered. Firstly, the surface of a solid electrode is not uniform and electrodeposition on different portions of the surface proceeds

at a different rate. Secondly, in the process of deposition the activity of separate portions of the electrode surface may change with time. All this is the cause of poor reproducibility of the results in studying the electrodeposition of metals and makes it difficult to establish strict quantitative laws.

Part of these difficulties can be overcome if we investigate the discharge of metal ions on a liquid (mercury) electrode having a homogeneous surface. The results of such investigations show that the ions of metals forming amalgams are reduced on a mercury electrode at a considerable rate. For this reason the polarization phenomena observed are mainly due to concentration polarization. At the same time ions of the metals of the iron group ($Fe^{2+}$, $Ni^{2+}$, . . .) that do not form amalgams are reduced on mercury with a great overvoltage. In this case the latter is due either to the fact that these metals owing to their low solubility in mercury are liberated in a highly dispersed state rich in energy, or to the fact that the discharge of these ions is retarded. The latter circumstance is confirmed by the fact that modern accurate experimental methods have made it possible to establish that the ions of zinc, manganese, chromium and other metals dissolving in mercury with the formation of amalgams also discharge slowly on mercury. In addition, in the liberation of metals of the iron group on solid electrodes in conditions excluding the appearance of a highly dispersed state, discharge of the ions also occurs with a considerable overvoltage.

The rate of the process of electrical reduction of metals on a solid metal surface can be determined by one of the following steps: (1) slow discharge of the solvated ions, consisting in the transfer of the ions from the solvated state in the Helmholtz layer into the metal phase; (2) slow formation of the crystalline phase. The second step consists of two processes—the formation of a two-dimensional crystal seed on the surface of an electrode and growth of the crystals that have already formed. Each of these processes may proceed slowly.

Indeed, the chemical potential $\mu$ of a substance in the state of a small seed in equilibrium with the solution is greater than the chemical potential $\mu_0$ of the substance in the bulk of the metal phase. In the electrodeposition of a metal this results in an overvoltage whose magnitude can be related to the difference $\mu - \mu_0$ by the equation

$$\mu - \mu_0 = zF\eta \tag{24.20}$$

Since $\mu - \mu_0$ depends on the magnitude of the seed, Eq. (24.20) makes it possible to establish the relation between the dimensions of seeds and the magnitude of the polarization upon its appearance.

At the same time the growth of crystals that have already formed is accompanied by the process of diffusion of atoms deposited on the surface of the metal from the place of their deposition to the place

where the ions find their sites in the crystal lattice and are bound in it (the so-called process of migration of ions along the surface). This process frequently proceeds so slowly that its rate determines the kinetics of the entire process of electrodeposition.

When the rate of the process is determined by discharge of the ions, or the rate of growth of the crystals is small in comparison with the rate of formation of new centres of crystallization, the most dense and stable galvanic coatings are obtained in electrodeposition.

**24.9. Reactions of Electrolytic Reduction and Oxidation.** Electrochemical reactions, except for the simplest reactions of electrolytic oxidation and reduction (electrolytic dissolving or the formation of a metal phase) are exceedingly complicated ones.

This can be seen on the example of the reaction of discharge of hydroxonium ions considered above. This reaction seems to be one of the most simple ones, but its mechanism is quite complicated. Electrochemical reactions with the participation of organic molecules are still more complicated. In this connection, and also owing to the absence of sufficiently effective complex methods that would allow us to grasp all the intermediate steps of a complicated electrochemical process even partly, our information on the true mechanism of reactions of electrolytic reduction and oxidation is quite sparse.

Up to recently the general accepted notions were that electrolytic reduction and oxidation, in particular of organic compounds, take place at the expense of atomic (adsorbed) hydrogen or oxygen formed on the electrodes in electrolysis. According to these notions an electrochemical process consists in the formation of atomic oxygen or hydrogen, while the process of electrosynthesis proper is considered to be an ordinary chemical process of hydrogenation or oxidation.

If this is true, we may expect complete analogy between, for example, electrolytic reduction and ordinary catalytic hydrogenation on the corresponding metals. Indeed, S. Fokin showed (1905) that the process of electrolytic reduction of certain unsaturated organic compounds proceeds the easiest on metals of the platinum group which, as is known, are typical catalysts in the hydrogenation of these substances by molecular hydrogen. In a further series of investigations on electrolytic reduction, it was proved that if we use metals well adsorbing hydrogen as electrodes, many organic compounds are indeed reduced by the adsorbed hydrogen. It should be remembered, however, that in this case the process is much more complicated than in ordinary hydrogenation, and includes intermediate, in particular electrochemical, steps.

The study of the mechanism of a complicated process consists to a considerable degree in establishing the limiting step. If electrolytic reduction proceeds even via adsorbed hydrogen, the limiting step may be a purely electrochemical one. In this case the sum-

mary process will obey not chemical, but electrochemical laws. For example, the process of electrolytic reduction of an organic compound in the simplest case will consist in the following two steps:

$$2H_3O^+ + 2e \rightarrow 2H\,(ads.) + 2H_2O$$
$$2H\,(ads.) + R \rightarrow RH_2$$

where R is a molecule of an organic compound.

If the rate of the first step is less than that of the second one, then although the reaction does proceed via adsorbed hydrogen, the rate observed will be determined by that of discharge of the hydroxonium ions and will obey the laws characteristic of this electrochemical reaction.

It is known that many reactions of electrolytic reduction easily proceed on mercury, lead and other metals that do not practically adsorb hydrogen. It is clear that in this case electrohydrogenation, i.e. hydrogenation by the adsorbed hydrogen, is impossible. It is natural to assume that on these metals the first step of the process of electrolytic reduction or oxidation is the direct attachment of an electron to the corresponding molecule or the detachment of an electron from it. The mechanism of such a reaction is called an electron mechanism.

The well studied reaction of electrolytic reduction of molecular oxygen on a mercury electrode can serve as an example of such a process. It has been proved that the primary step is the direct attachment of an electron of the electrode to an oxygen molecule:

$$O_2 + e \longrightarrow O_2^- \qquad (1)$$

with the formation of a molecular ion of oxygen. Owing to the lack of stability of this ion in aqueous solutions, its detection is not successful. But $O_2^-$ can be considered as an anion of the acid $HO_2$, solid salts of which ($KO_2$, $NaO_2$) are known.

The ion $O_2^-$, having an odd number of electrons, is unstable and reacts, for example, in an acid medium according to the scheme

$$O_2^- + H_3O^+ \longrightarrow HO_2\cdot + H_2O \qquad (2)$$
$$HO_2\cdot + e \longrightarrow HO_2^- \qquad (3)$$
$$HO_2^- + H_3O^+ \longrightarrow H_2O_2 + H_2O \qquad (4)$$

It has been found that the slowest (limiting) step is the first one, i.e. the attachment of an electron to the molecule $O_2$.

An electron mechanism has also been established for the electrolytic reduction of the anion $S_2O_8^{2-}$, which proceeds according to the equation

$$S_2O_8^{2-} \xrightarrow{2e} 2SO_4^{2-}$$

Among organic reactions that of electrolytic reduction of oxalic acid has been well investigated. It proceeds according to the equ-

ation

$$(COOH)_2 + 2H^+ \xrightarrow{2e} COOH-CHO + H_2O$$

In this case also the limiting step is the attachment of an electron to a molecule of oxalic acid:

$$(COOH)_2 + e \rightarrow (COOH)_2^-$$

after which the further transformations proceed at a great rate.

One of the most important reactions from both a theoretical and a practical standpoints is that of the electrolytic reduction of nitrobenzene. Although it has been investigated for scores of years and the number of works devoted to it is very great, its mechanism has not been exactly established to date owing to the exceedingly complicated nature of this process.

The main intermediate steps are as follows:

$$C_6H_5NO_2 \xrightarrow{2e} C_6H_5NO \xrightarrow{2H^+} C_6H_5NHOH \xrightarrow{2e} C_6H_5NH_2$$

Owing to the difference between the rates of the separate electrochemical steps and to the purely chemical interaction of the intermediates between one another and with the reactant, however, different products are obtained on different cathodes and in different electrolytes (in addition to those indicated above, the products include azoxybenzene, azobenzene, hydrazo-benzene, benzidine and *p*-aminophenol).

In recent years great attention has been devoted to the investigation of electrochemical processes that proceed with the participation of one electron and are accompanied by dimerization of the radicals formed. An example of such reduction dimerization on an electrode is the preparation of pinacol from acetone:

$$CH_3COCH_3 \xrightarrow{e+H^+} CH_3\dot{C}(OH)CH_3$$

$$2CH_3\dot{C}(OH)CH_3 \rightarrow (CH_3)_2C(OH)-C(OH)(CH_3)_2$$

According to the notions accepted at present, electrolytic oxidation may proceed either with the aid of intermediate oxidizers—adsorbed oxygen, oxygen compounds of metals and free hydroxyl formed in the discharge of the $OH^-$ ions, or by detaching an electron from the molecule being oxidized itself. Thus, it has been shown that the mechanism of electrolytic oxidation of sulphate ions into persulphate ions is an electron one:

$$SO_4^{2-} - e \rightarrow SO_4^-$$

$$2SO_4^- \rightarrow S_2O_8^{2-}$$

**24.10. Passivity of Metals.** If a metal is immersed into a solution containing ions of the same metal, then, as is known, electrochemical equilibrium sets in on the surface of the metal electrode and the

corresponding electrode potential appears. When a current is passed through the solution, this equilibrium is violated. Depending on the direction of the current, an electrode process appears that tends to restore equilibrium. In cathode polarization, i.e. when electrons are supplied to an electrode, the process of electrocrystallization occurs, i.e. the transition of metal ions from the solution into the crystal lattice. In anode polarization, i.e. when electrons are removed from the electrode, electrolytic dissolving of the metal occurs, i.e. destruction of its crystal lattice and transfer of the lattice ions into the solution.

Frequently both these processes (electrocrystallization and anode dissolving of the metal) proceed sufficiently rapidly and are not accompanied by appreciable overvoltages. For example, if we immerse two copper plates into a solution of blue vitriol and pass a current through it, then even at a low voltage electrolytic dissolving of the anode occurs and copper is deposited on the cathode. As is known, this underlies electrical refining (the purification of copper by electrolysis).

For a number of metals (Fe, Cr, Ni, Mn) the process of anode solution proceeds at a low rate and is accompanied by great overvoltages.

Metals of transition groups are characterized by a greatly reduced ability of solution in acids and of anode dissolving after the surface of these metals has been treated with oxidizers. Such a state of metals is called *passivity*. For chromium, gold and platinum the action of the oxygen of the air is sufficient for these metals to become passive. If iron is immersed in concentrated nitric acid, it becomes passive and does not dissolve in dilute nitric acid. Iron, chromium, nickel and other metals can be transferred into a passive state by treating them with oxidizers, for example by immersion into a solution of bichromates, nitrates, etc.

If in anode dissolving of metals a potential is applied to the anode that exceeds a certain definite value, then the metal also becomes passive.

Passivated metals have different chemical and electrochemical properties than metals in the ordinary active state. Passive iron does not displace copper from solutions of its salts. Active chromium forms $Cr^{3+}$ ions in a solution, passive chromium—$CrO_4^{2-}$ ions. Manganese behaves in a similar way. The passivity of metals can be eliminated by the action of reducers, and sometimes by heating or scraping off the surface layer. Cathodic polarization of a metal, i.e. the imparting of a negative charge to it, also almost always activates metals. For this purpose it is sometimes sufficient to create a cell by contacting a more negative metal with the passive one in a solution (for example, zinc or magnesium with iron).

It should be noted that passivity does not stop the process completely, but only greatly retards it.

Thus a passive state can be achieved both chemically and electrochemically, but only on condition that oxygen is present and acts in some way. Already from M. Faraday's time this circumstance was related to the idea that chemically bound oxygen appears on the surface of a metal, as a result of which the interaction between the metal and the solution stops or is hampered.

The plausibility of this assumption is confirmed by the fact that the activity of a metal can be restored by cathodic polarization, when the oxide film is mainly destroyed by the liberated hydrogen. G. Akimov showed that simple mechanical scraping of a passive metal surface under a solution makes the metal active and causes the potential to shift in the negative direction.

The assumption that the cause of passivity is the formation of a protective oxide film on a metal was a hypothesis for a long time, since investigators did not succeed in proving the existence of this film experimentally. In appearance active and passive metals are identical. Even x-ray photographs do not show a difference between them.

A considerable part in the development of the modern theory of passivity of metals belongs to V. Kistyakovsky, U. Evans, N. Izgaryshev, G. Akimov and others. Using Faraday's ideas as a foundation and employing more refined modern methods of investigation, they were able to prove the truth of the assumption that an oxide film is present on passive metals, and also later to develop conceptions of passivating films (not necessarily oxide ones) as the causes of passivity.

The difficulty of experimental detection of an oxide film was found to be due to the insignificant thickness of this film. For this reason, in particular, the radiographic method, which owing to the high penetrating ability of x-rays makes it possible to examine the picture of a surface layer 100 and more angstroms thick, was found to be too crude.

P. Dankov used the more refined electron-diffraction method of investigation. Owing to the fact that electrons do not penetrate into a metal, but are dispersed by the surface layers, this method makes it possible to obtain a notion on the state of the surface layer. Electron-diffraction patterns show a clear difference between the structure of the surfaces of active and passive metals. In particular, it was established that upon the passivation of nickel, NiO is formed on it, of iron—$\gamma$-$Fe_2O_3$, of aluminium—$Al_2O_3$. The thickness of the oxide layers is only several scores of angstroms.

These results were later confirmed by investigations on electronic emission and the photoelectric effect.

Having proved the presence of an oxide film on a passive metal, V. Kistyakovsky developed the notions of passivating films as the causes of passivity and showed that they must not necessarily be

oxygen ones. Thus, the passive state of lead may be caused by the formation on its surface of the salt $PbSO_4$. On certain metals (for example, silver) the film may be a halide (AgCl).

Passivating films are not always formed by chemical compounds. Frequently passivity is observed upon the adsorption of various substances, especially organic ones.

There is no doubt that a film on a metal surface is the cause of its passivity. Different opinions exist, however, on the structure and action of this film. The most widespread one is that a continuous film exists which completely screens the surface and thus isolates the metal from its surroundings. Ions of the metal and electrons slowly diffuse through the film. For this reason the rate of reaction is very low and is limited by the rate of diffusion. In a number of cases the formation of such continuous films has been proved ($Al_2O_3$), and for these cases the mechanical theory of passivating action is correct.

It was established comparatively recently that a passivating film must not necessarily be a continuous one. Thus, the presence on a platinum surface of oxygen occupying only a small fraction of the total surface area of the metal results in the almost complete stopping of the anodic dissolving of platinum in hydrochloric acid. It can be assumed that anodic dissolving and in general the interaction of a metal with aggressive media proceed not over its entire surface, but only on a relatively small number of little portions of the surface, i.e. the notion of active centres having such a great significance in the theory of catalysis also remains in this case.

**24.11. Corrosion.** The process of spontaneous destruction of metals under the influence of the surroundings is called *corrosion*.

*Chemical* and *electrochemical* corrosion is distinguished.

Chemical corrosion occurs when various substances (liquids, non-electrolytes and gases) act on metals at high temperatures. It has a great significance in all the fields of activity of mankind. It includes the oxidation of iron in air at elevated temperatures with the formation of scale.

Below we shall discuss electrochemical corrosion. It is exceedingly widespread, since it frequently proceeds at a considerable rate at ordinary temperatures, when chemical corrosion does not practically manifest itself.

Electrochemical corrosion occurs when a metal or metal alloy comes into contact with a liquid conducting electricity, for example soil water, water in steam boilers, and especially with various reactive media, mainly in the chemical industry.

The presence of a thin film of liquid on the surface of a metal is sufficient for electrochemical corrosion to become possible. This type of corrosion is characterized by the appearance of electrical

currents between different parts of the metal (motion of electrons) that are a result of electrochemical reactions on separate portions of the surface of contact of the metal with the electrolyte.

The solution of a metal in acids can also be considered as electrochemical corrosion. Let us consider the solution of zinc in an acid:

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

This equation reflects the summary process. The essence of the process, however, consists in that the metal zinc immersed into a solution of an acid comes into equilibrium with this solution in such a way that a certain number of ions $Zn^{2+}$ passes into the solution, and the electrode acquires a negative charge. An electrical double layer is formed whose surface in the solution attracts both zinc ions and hydroxonium ions. The potential of the electrode is sufficiently high for the hydroxonium ions to discharge, taking up electrons from the surface of the electrode. The equilibrium potential is retained by the solution of new quantities of $Zn^{2+}$.

Thus, when zinc is immersed into the solution, two different parallel, though conjugated, electrochemical processes proceed simultaneously:

$$Zn\ (\text{met.}) + nH_2O \longrightarrow Zn^{2+} \cdot nH_2O\ (\text{in solution}) + 2e$$

$$2H_3O^+ + 2e \longrightarrow 2H_2O + H_2$$

For this reason the self-solution of zinc in acids should not be considered as a chemical reaction of displacement of hydrogen by the zinc (the elementary acts are different).

Since corrosion is accompanied by the removal of electrons from the surface of metals, it can proceed not only under the action of discharging ions of hydroxonium (as in the example with zinc), but can be the result of the action of any oxidizers that are acceptors of electrons. For example, the self-solution of metals is greatly accelerated in the presence of oxygen of the air in the solution, since the following reaction proceeds on the surface of the metal:

$$\frac{1}{2} O_2 + 2e + H_2O \longrightarrow 2OH^-$$

This reaction proceeds at a more positive potential than the discharge of the hydroxonium ions. For this reason anodic dissolving of metals is as it were a particular case of corrosion, when the electrons are removed from a surface by a current.

To explain corrosion, C. De la Rive (1830) put forward the idea of local cells forming on the surface of a metal immersed into a liquid[1].

[1] Russian and Soviet scientists made a great contribution to the development of the theory of electrochemical corrosion.

N. Kayander (1880) put forward the idea of the electrochemical nature of the solution of metals. In 1881 N. Sluginov made the first attempt to describe

The formation of a local cell can be imagined in the simplest way taking as an example the contact of two metals, each of which is also in contact with a liquid conducting electricity. For example, when copper and iron come into contact, a short-circuited cell is formed. Its soluble pole is the iron, since electrons flow from iron to copper. Solutions in nature usually contain the ions $H_3O^+$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$, and also dissolved oxygen. Of these ions, practically only the hydroxonium ions can discharge, while the oxygen can be reduced with the formation of the ion $OH^-$.

When metals come into contact, the electrons pass from the electrically more negative metal to the more positive one. As a result the former will dissolve, and hydroxonium ions will discharge or the dissolved oxygen will be reduced on the latter. This is a case of so-called *contact corrosion*. This kind of corrosion may occur on one metal at places subjected to different processing, or with different foreign inclusions, especially metallic ones. In this case specific microcells are formed whose circuits are closed through the basic metal. The "functioning" of these cells intensifies ordinary corrosion.

The existence of local microcells was proved experimentally by Akimov, who with the aid of a fine capillary filled with a solution measured the distribution of the potential along the surface of the metal or alloy. He showed that the potential differences between separate parts of the surface are usually equal to several millivolts.

It was established that corrosion also occurs spontaneously on a homogeneous surface. Hence it cannot be related only to the action of local cells. The presence of such cells only intensifies corrosion.

A. Frumkin developed the electrochemical theory of metal corrosion. He showed that the electrochemical reactions indicated above leading to corrosion (transition of metal ions into a solution and the reaction of reduction of hydrogen or another oxidizer-depolarizer, for example of oxygen) may proceed with the same potential on the same portion of the surface of a metal. Calculations of the potential in agreement with experimental data point to the very small difference between separate portions of the surface of a metal.

It should be noted that the problem of protection against corrosion cannot be solved without considering a certain relation of corrosion to passivity. If corrosion is a process of spontaneous dissolving of metals, then passivation is connected with a metal losing this property. Consequently, to protect a metal against corrosion it must be transferred into a passivated state.

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this phenomenon quantitatively. He related the rate of corrosion with the e.m.f. and resistance of the local cells.

The further development of the theory of electrochemical corrosion is associated to a considerable extent with G. Akimov, who gave the modern interpretation of these phenomena, mainly on the basis of conceptions of local cells.

Some metals are passivated in oxidizing media, for example iron in concentrated nitric and sulphuric acids. This is why these acids are stored in iron tanks. Iron, nickel, cobalt and magnesium are also passive in alkaline solutions.

Stainless steels, which in addition to iron contain chromium, nickel, manganese and small amounts of titanium and niobium, are stable to corrosion. Under the action of air and water a chemically and mechanically strong oxide film forms on articles made from such alloys. It completely passivates the metal.

If insoluble products are formed when a metal dissolves (for example, lead in sulphuric acid), their deposition on the surface may inhibit or completely stop corrosion.

Such passivation can be called "mechanical" in contrast to "chemical" passivation due to the chemical adsorption of oxygen mentioned above.

It must be noted that depending on the external conditions and the nature of a metal, the action of the same substances may either accelerate or inhibit corrosion. As previously indicated, the presence of oxygen of the air in a solution frequently accelerates corrosion owing to electrolytic reduction of the oxygen according to the reaction $O_2 + 4e + 2H_2O \rightarrow 4OH^-$, in the course of which electrons leave the metal and the ions of the latter pass into solution. If an oxide film is formed easily or insoluble products form in corrosion, the oxygen may inhibit corrosion instead of accelerating it (for example, the corrosion of aluminium and zinc in air).

Corrosion occurs to a smaller extent in neutral and alkaline solutions not only because the concentration of hydroxonium ions is lower in these solutions, but also because passivating films of a basic nature are formed in them more easily.

Chloride, bromide and iodide ions, as a rule, are depassivators of stainless steels and chromium in acid and neutral media, and of nickel and iron in alkaline ones. Consequently these ions promote corrosion.

Recent years have seen the widespread introduction of various well adsorbed substances (inhibitors), frequently organic compounds, for inhibiting corrosion.

Being adsorbed on the surface of a metal, inhibitors can appreciably reduce the rate of electrochemical reactions resulting in corrosion. Halide ions in acid solutions facilitate the adsorption of a number of organic compounds (mainly nitrogen-containing organic bases) on the surface of iron and soft steels and, therefore, intensify the retarding action of the inhibitors.

A protective anticorrosion layer is frequently formed by applying a continuous layer of stable paint or another metal. In the latter case a less noble metal will have a better protective action. For example, it is better to cover iron with zinc than with copper. This

is explained by the fact that upon local violations of the coating, the less noble metal will be subjected to corrosion, since at the place of violation of the continuous film a cell will appear in which the electrons pass from the less noble metal to the more noble one, and as a result the former will dissolve.

This phenomenon is widely used to protect water mains, steam boilers and in general metal structural members against corrosion. They are brought into contact with strips of a less noble metal, and thus corrosion of the basic metal is stopped.

**24.12. Polarography.** The method of studying electrochemical processes based on establishing the dependence of the current intensity on the voltage applied to the system being investigated is called *voltammetry*. The first form of voltammetry that was developed and the most accurate one is *polarography*.

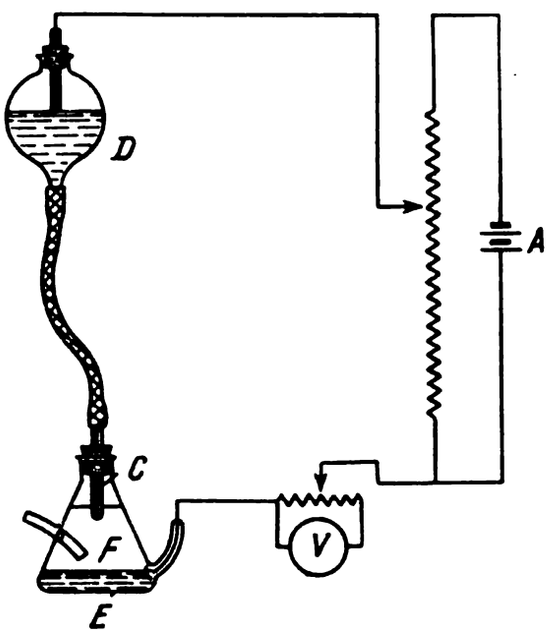


Fig. 24.4. Heyrovsky's polarograph:

*D*, *E*—electrodes; *C*—capillary; *F*—flask; *V*—potentiometer; *A*—accumulator

The polarographic method proposed by the Czech scientist J. Heyrovsky (1922) consists in conducting electrolysis of solutions being investigated in an electrolytic cell (electrolyzer), one of whose electrodes is a dropping mercury one. The latter may serve either as the cathode (in studying electrolytic reduction) or as the anode (in studying electrolytic oxidation).

A dropping mercury electrode (Fig. 24.4) is a glass capillary *C* through which mercury flows out under the pressure of the mercury column. The mercury drops formed at the end of the capillary break away from it at equal intervals (usually from 0.2 to 6 s) and drop onto the bottom of flask *F*. Each mercury drop up to the moment of its breaking away serves as an electrode. A definite voltage is applied to electrodes *D* and *E* of the polarographic cell by means of accumulator *A* and potentiometer *V*. A sensitive galvanometer measures the intensity of the current flowing through the system. In the general case the potentials of both electrodes change when a current flows through the cell. In addition, part of the applied voltage drops in the solution:

$$E = \varphi_A - \varphi_C + IR$$

where $E$ = external potential difference
$\varphi_A$ and $\varphi_C$ = potentials of anode and cathode, respectively

$I$ = current intensity
$R$ = resistance of solution. .

Generally a mercury electrode with a great surface area whose potential does not practically change when a current of a small density is passed through it is used as an auxiliary electrode in polarographic measurements. A sufficient amount of an indifferent electrolyte that ensures a high conductivity of the solution is added to the solution being investigated (placed in flask $F$). Thus

$$E = -\varphi_C + \text{const}$$

The change in the potential difference applied from an external source in making the measurements as indicated above is therefore equal to the change in the potential of the dropping electrode.

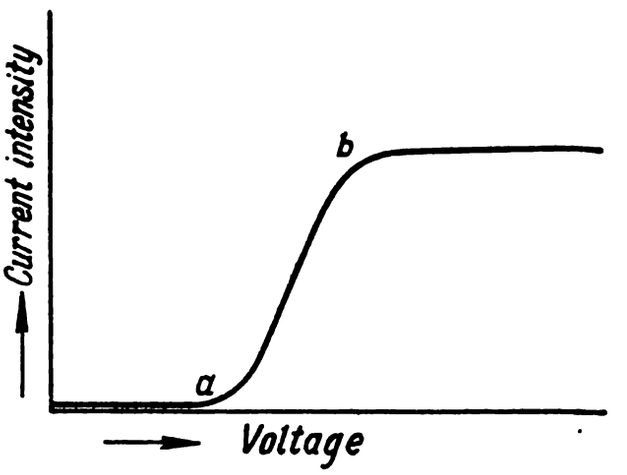

Fig. 24.5. Polarization curve

Upon a gradual increase in the external potential difference, first the entire current goes to charge the electrode (the electrical double layer). Hence the intensity of the current in the circuit remains vanishingly small, which points to the absence of an electrochemical process (Fig. 24.5). After a definite potential difference has been reached (point $a$) a sharp growth in the intensity of the polarizing current occurs. This indicates the beginning of an electrochemical process of electrolytic reduction or oxidation. As the potential of the electrode and the current intensity grow, the concentration of the particles being reduced or oxidized near the surface decreases, and concentration polarization sets in. Finally, upon an increase in the polarization, the concentration of the particles at the surface of the electrode drops to zero, and the current reaches its maximum value (point $b$). Thus a polarization curve, i.e. a current-potential curve, has the shape of a wave. This curve is called a *polarographic curve* or a *polarogram*. The beginning of the wave corresponds to the beginning of the reaction of oxidation or reduction, and the height of the wave determined by the magnitude of the maximum current characterizes diffusion of the substance to the electrode. Owing to the fact that the rate of diffusion is proportional to the bulk concentration, the wave height is directly related to the concentration of the reacting particles. This allows the polarographic method to be used for the quantitative analysis of complicated electrolytes. The potential at which the current reaches half of the maximum diffusion current is called the *half-wave potential*. The magnitude of this potential depends only on the nature of a separate reactant, and determination

of the half-wave potentials on a polarogram makes it possible to appraise the qualitative composition of the solution being analysed. If a solution simultaneously contains several species of ions that can be reduced, then the polarization curve has the form shown in Fig. 24.6. The current grows in pulses, the reduction of each cation being reflected by a separate wave on the polarogram. The presence of three waves on the given polarogram shows that there are three different species of cations in the solution. The nature of the cations is established according to the half-wave potentials, and their concentrations according to the height of the corresponding waves.

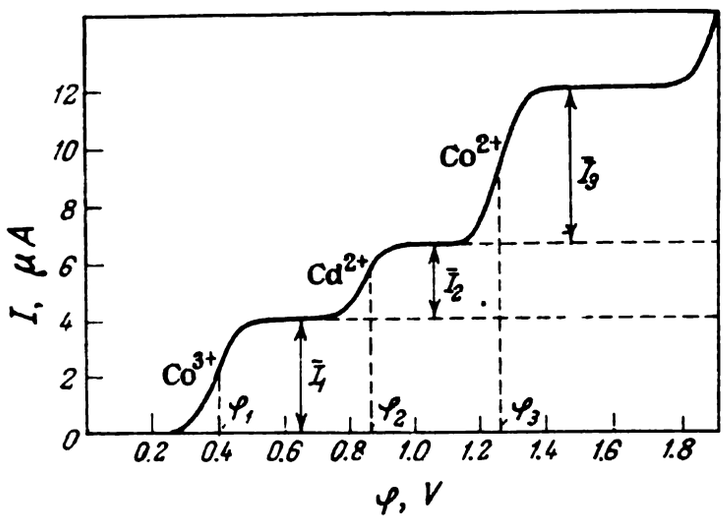


Fig. 24.6. Polarogram

Let us consider in greater detail the phenomenon of concentration polarization on a dropping mercury cathode upon the discharge of ions of a metal, for example cadmium. In contrast to the example of the reduction of silver ions on a silver electrode considered above, where the nature of the metal does not change in the process of electrolysis, the discharge of cadmium ions on the mercury cathode is accompanied by the formation of a cadmium amalgam. The potential of the amalgam electrode

$$E = E^\circ + \frac{RT}{zF} \ln \frac{c_s}{c_{s,\,Me}} \qquad (24.21)$$

where $c_{s,\,Me}$ = concentration of the cadmium amalgam at the surface of the electrode

$c_s$ = concentration of the cadmium ions in the solution at the surface of the electrode.

Thus, to find an equation for the concentration polarization on a dropping mercury electrode, the dependence of the quantities $c_s$ and $c_{s,\,Me}$ on the current has to be determined. The process of diffusion to a growing spherical surface is much more complicated than the same process to a stationary solid electrode. Since the surface area of a drop continuously grows during the period of its existence and, therefore, the current flowing through the drop into the solution grows, the concept of the average current $\bar{I}$ during the life of a drop is introduced. As shown by accurate calculations, the magnitude of the average diffusion current on a dropping mercury electrode is

$$\bar{I}_d = 0\,627 zFD^{1/2} m^{2/3} \tau^{1/6} (c_b - c_s) = \varkappa (c_b - c_s) \qquad (24.22)$$

where $c_b$ and $c_s$ = concentrations of the cadmium ions in the bulk of the solution and at the surface of the electrode, respectively, mol/cm³

$m$ = rate of flow of mercury, mg/s

$\tau$ = drop life, s

$\varkappa$ = factor that is constant at given conditions of functioning of the electrode.

The average maximum diffusion current is expressed by the equation

$$\overline{I}_d = \varkappa c_b \tag{24.23}$$

Equations (24.22) and (24.23) are called the *Ilkovič equations* and are used in quantitative polarographic analysis.

Equations (24.22) and (24.23) allow us to determine the value of $c_s$:

$$c_s = \frac{1}{\varkappa}(\overline{I}_d - I) \tag{24.24}$$

Since an amalgam is formed on the surface of the mercury, a current appears in the drop itself that flows inward from the surface. It can be shown that the magnitude of the average diffusion current inside the mercury drop is determined by an equation that coincides in form with Eq. (24.22):

$$\overline{I} = 0.627 zFD_{Me}^{1/2} m^{2/3}\tau^{1/6}c_{s,\,Me} = \varkappa_{Me}c_{s,\,Me} \tag{24.25}$$

where $D_{Me}$ and $c_{s,\,Me}$ relate to the atoms of the metal dissolved in the mercury. The value of $c_{s,\,Me}$ can be found from Eq. (24.25).

Using Eqs. (24.24) and (24.25) in Eq. (24.21), we get an expression for the concentration polarization on a dropping mercury electrode:

$$E = E_{1/2} + \frac{RT}{zF}\ln\frac{\overline{I}_d - I}{\overline{I}} \tag{24.26}$$

or for the magnitude of the average current

$$\overline{I} = \frac{\overline{I}_d}{1 + e^{\frac{zF}{RT}(E - E_{1/2})}} \tag{24.27}$$

where

$$E_{1/2} = E^\circ + \frac{RT}{zF}\ln\frac{\varkappa_{Me}}{\varkappa} = E^\circ + \frac{RT}{zF}\ln\frac{D_{Me}^{1/2}}{D^{1/2}} \tag{24.28}$$

A glance at Eq. (24.28) shows that the half-wave potential $E_{1/2}$ depends only on the value of the standard potential of the electrode and the ratio of the diffusion coefficients of the metal atoms in the amalgam and the metal ions in the solution. It is therefore a quantity that depends only on the nature of the reacting ion.

The polarographic method of analysis has a number of advantages over other methods. It can be used for very complicated systems and with a great saving of time, since a polarogram can be obtained in several minutes. Since the surface area of a mercury drop is very small, the polarizing current is negligible ($10^{-5}$ to $10^{-6}$ A) and does not practically change the concentration in the bulk of the solution. For this reason several polarograms can be obtained for the same solution. This method gives reliable results at concentrations up to $10^{-5}$ mol/dm$^3$ (from 0.1 to 0.2 cm$^3$ of a solution is sufficient for analysis), i.e. it is very sensitive. A polarogram can be recorded automatically or obtained on the screen of an oscillograph.

The polarographic method is also used for determining many organic compounds and even dissolved gases (for example, oxygen). In addition, polarography is an important method for investigating the kinetics and mechanism of electrode processes.

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